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Master's degree Thesis in
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Electroreduction of CO_2 into chemicals with Deep Eutectic Solvents as an electrolyte

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ABSTRACT

The objective of this thesis is to investigate the carbon dioxide absorption process, which is produced in enormous quantities by anthropogenic resources such as, cement production, fossil fuel combustion processes and the decomposition of organic substances, is considered as the major contributor to greenhouse gases.

What is worrying is that in the years between 2000 and 2010, the concentration of CO2 in the atmosphere exceeded the threshold limit values. Finding an optimal solution for the abatement/capture of this substance is now of paramount importance.

The study is organized into two distinct sections.

The initial part focused on the development and characterization of deep eutectic solvents, DESs, both prior to and after carbon dioxide absorption. This entails a detailed examination of the experimental setup and the formulation of models to describe critical parameters for various solvents. This experimentation extends to the investigation of the absorptive properties of the examined solvents at different operating temperatures—specifically, 25, 35, and 45 degrees Celsius. Additionally, the study explores the absorptive capacities of DES with identical components but varying molar ratios. The comparative study between DES for chemical and physical absorption was also carried out. The thermodynamic model is examined using the Reaction Equilibrium Thermodynamic Model (RETM), which breaks down absorption into chemical and physical categories, extracts equations, and combines them to assess the overall CO2 absorption. The characterization phase seeks to visually confirm the interaction between CO2 and the solvent. To achieve this, FTIR and NMR analyses were conducted. Additionally, the characterization part includes the calculation of critical properties.

The subsequent section explores the electrochemical conversion of carbon dioxide absorbed within these solvents, leading to the generation of products containing carbon atoms. This section provides a comprehensive overview of the experimental setup and the various characterization tests conducted. This section provides a detailed explanation of the synthesis of the working electrode, composed of cobalt-doped carbon paper with nitrogen-carbon nano dots (N-CND). These nano dots are directly synthesized from spruce needles and twigs, serving as a catalyst in the electroreduction process in the current study. In this study, the desired process has been achieved: the conversion of CO2 into valuable products, specifically CO.

At the conclusion of the study, the findings and conclusions pertaining to the described topic are presented.

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INTRODUCTION

In the current context, the growing importance of CO2 emissions in the atmosphere underlines the imperative to reduce this excess in the air. Substantial efforts are underway to mitigate the negative impact of excess carbon dioxide in the atmosphere. One prominent strategy involves the absorption of CO2 in studied solvents, which is a powerful approach to reduce its high concentration.

The absorption process can be classified into two distinct methods: chemical absorption and physical absorption. Chemical absorption involves the formation of stronger bonds, leading to the creation of more durable components. Physical absorption, on the other hand, involves the formation of weaker bonds, resulting in the generation of less persistent compounds. This duality in absorption mechanisms allows us to understand how CO2 can be effectively sequestered.

Beyond its role in decreasing the volume of this pollutant, CO2 adsorption serves as the initial step in a broader initiative to convert it into refined and valuable compounds. This transformative approach seeks to extract value from an apparently insubstantial compound, thus turning a virtually worthless substance into a source of tangible benefits. Using absorption not only as a means of reduction, but as a precursor to converting CO2 into valuable products, we undertake a study to reuse and extract value from a once seemingly intractable environmental challenge. The utilization of deep eutectic solvents has made a significant contribution to this specific task. These solvents offer several advantages over traditional ones, including a wide liquid range, high thermal stability, and high absorption rates. However, what is particularly intriguing is that they are formed from environmentally benign compounds.

The objective of this thesis is to assess the absorptive capacities of five imidazole-based deep eutectic solvents in terms of chemical absorption, and two deep eutectic solvents in terms of physical absorption. Initially, the absorbent capacity is evaluated through a simple absorption test, wherein the deep eutectic solvent (DES) is introduced into an equilibrium reactor, and with temperature held constant. Utilizing the ideal gas law, the absorbed CO2 can be calculated as a function of temperature. Additionally, the influence of temperature on the absorbent capacity is examined by conducting the CO2 absorption at three different temperatures using the same method. The Reaction Equilibrium Thermodynamic Model is employed as a thermodynamic model to compute the quantity of CO2 absorbed in both chemical and physical absorption.

The other facet of this research involves characterizing these solvents to visually understand the interaction between CO2 and the various solvents. For this purpose, FTIR analysis, NMR analysis, and viscosity analysis are conducted. In addition to this characterization, critical properties are calculated to gather more insights into the created deep eutectic solvents (DES).

The second phase of this project focuses on the electroreduction aspect, employing a conventional H-type electrocatalytic cell for the reduction of CO2. Deep eutectic solvents (DES) serve as the electrolyte in this process, facilitating the movement of electrodes within the cell. The experimental setup involves three electrodes: the counter electrode, made of platinum sheet material; the reference electrode, composed of Ag/AgCl; and, most notably for this study, a working electrode synthesized from spruce needles and twigs supported by cobalt-doped carbon paper (Nitrogen-Carbon Nano Dots on cobalt doped carbon paper). The latter electrode is crucial for its catalytic effect on the process, thereby expediting the overall reduction process. At the conclusion of the experiments, verification tests for CO2 conversion will be conducted.

The study is subdivided into three chapter:

1. Chaper 1: It provides information on deep eutectic solvents, delving into the specifics of electroreduction and offering a comprehensive overview of the CO2 issue. Subsequently, the experimental setups for the two distinct parts of the project are explained.
2. Chapter 2: This section pertains to the experimental part, providing a detailed explanation and listing of the chemicals involved in this study, along with all the analysis equipment utilized. Subsequently, the thermodynamic model and the study of critical properties are elaborated in detail, including the relevant formulas and explanations.
3. Chaper 3: In this chapter, a comprehensive and detailed analysis is conducted on all the results obtained throughout the various stages of this study. The chapter is divided into two parts: the first part focuses on the formation and characterization of deep eutectic solvents (DES) and the examination of absorption tests, while the second part delves into the analysis of choosing the optimal electrode for electroreduction and the scrutiny of the electroreduction results.

This project was conducted at the Chemistry Department of Umea University, within the research group led by Professor Jiry Pekka Mikkola. The experimental tests were performed under the supervision of Dr. Shokat Sarmad and Dr. Gopinathan Malavan. The final phase of the project, involving the comparison of results and thesis writing, took place at the University of Padova under the guidance of Professor Paolo Canu.

CHAPTER 1

INTRODUCTION AND EXPERIMENTAL SET-UP

In this initial chapter, an introduction is provided to the prior work conducted by other researchers in this specific field. All necessary background information for the conducted study is presented, and a comprehensive explanation of the experimental setup is provided, given its utilization in various other studies.

1.1 Deep Eutectic Solvents and CO_2 absorption

1.1.1 Problem of CO_2

Given the paramount significance of addressing greenhouse gas emissions in combatting global warming and climate change, it becomes evident that mitigating these emissions stands as one of the most pressing global challenges of our time. Among the various greenhouse gases, carbon dioxide (CO_2) takes center stage due to its substantial production from anthropogenic sources, such as cement manufacturing, fossil fuel combustion processes, and the decomposition of organic materials. It is, by far, the most significant contributor to the greenhouse gas effect.

What raises alarm is that, during the decade spanning from 2000 to 2010, the concentration of CO_2 in the Earth's atmosphere exceeded the critical threshold value of 350 parts per million (ppm). This milestone marked a significant turning point, underscoring the urgency of finding optimal solutions for the abatement and capture of carbon dioxide. Addressing this issue is not only a scientific and technological imperative but a moral responsibility to safeguard our planet's climate and future generations from the adverse consequences of unchecked greenhouse gas emissions. Carbon capture and storage (CCS) stands as a pioneering technological approach aimed at effectively mitigating carbon dioxide (CO_2) emissions, a critical strategy in the ongoing battle against global climate change. The concept behind CCS involves capturing carbon dioxide emissions generated from various industrial and energy-related processes, transporting the captured CO_2 to a suitable storage site, and securely storing it to prevent its release into the atmosphere.

1.1.2 CCS techniques

In the quest to remove CO_2 from the atmosphere and industrial processes, several techniques have been explored, refined, and validated over the years. Among these, absorption, adsorption, and membrane technologies have emerged as some of the most promising solutions. These methods have undergone extensive research and development efforts, and they have now reached an advanced stage of innovation that holds the potential for a substantial reduction in the concentration of CO2 in the atmosphere.

The absorption process entails the capture of CO_2 by exposing it to a solvent or absorbent material that binds with the carbon dioxide, separating it from the emissions stream.

Adsorption, on the other hand, involves the use of solid materials, typically porous substances, to trap and hold CO_2 molecules, effectively removing them from the gas mixture. Lastly, membrane technologies leverage specialized membranes with selective permeability to allow the passage of CO2 while excluding other gases, facilitating its separation and capture. It is evident that CCS has the potential not only to mitigate emissions but to reshape the trajectory of our planet towards a more sustainable and climate-resilient future.

Currently, the predominant method for carbon dioxide (CO_2) capture relies on the process of absorption using liquid solvents. Among these solvents, aqueous alkanolamine solutions, with a particular emphasis on monoethanolamine, have garnered widespread use. This popularity can be attributed to their advantageous characteristics, including their high reactivity with CO_2, cost-effectiveness, ready availability, strong affinity for CO*2*, and low viscosity. However, it's important to acknowledge that this approach is not without its drawbacks, notably the corrosive and volatile nature of the amine compounds employed and, more significantly, the substantial energy demand required for solvent regeneration once it becomes saturated with CO_2.

Recognizing these challenges, considerable efforts have been dedicated to seeking more efficient alternatives for CO_2 absorption. A notable breakthrough in this regard has been the development and utilization of ionic liquids (IL) and, more recently, deep eutectic solvents (DES). These innovative solutions promise to overcome some of the limitations associated with traditional alkanolamine-based absorption methods.

Ionic liquids, with their unique properties and structure, offer a compelling alternative for CO_2 capture. Ionic liquids are compounds made up of a cation and an anion, in which an ionic bond is therefore present, with a melting temperature generally below 100°C.

They are non-volatile and non-corrosive, addressing the safety and environmental concerns associated with amine solvents. Furthermore, their customizable nature allows for the tailoring of specific ionic liquids to enhance their CO_2 absorption capacity and selectivity.

IL are expensive to be used in bulk application and it’s possible that the preparation for a specific IL is very expensive or raw materials are not green, which lead to an environmental hazard. They are moisture sensitivity and non-biodegradable. For these very reasons, it was decided to shift interest to a more sustainable and less expensive alternative, namely deep eutectic solvents.

1.1.3 Deep Eutectic Solvents

In recent developments, researchers have been exploring the potential use of DESs as agent for CO_2 separation. The field of solvent design and development has witnessed a growing interest in the exploration of deep eutectic solvents (DES) as environmentally friendly alternatives to conventional organic solvents. The eutectic properties of deep eutectic solvents are pivotal for several reasons. Foremost among these is their ability to achieve a low melting point, enhancing the versatility of these solvents across a broader spectrum of conditions. Additionally, the crucial attribute of remaining in a liquid state at room temperature is indispensable for practical applications.

Moreover, the eutectic nature imparts versatility to the solvents, allowing them to dissolve a wide range of compounds. This property is further accentuated by the tunability inherent in the eutectic composition, which enables customization of solvent characteristics by adjusting the ratio of components.

Notably, the eutectic property contributes to the environmentally friendly profile of deep eutectic solvents, aligning with green chemistry principles. This aspect, coupled with their biodegradability, renders them particularly intriguing for cutting-edge studies focused on the next generation of sustainable solutions.

Deep eutectic solvents represent a promising development in this field. DES are essentially a blend of two or more components that, when combined, form a liquid with properties favourable for CO_2 capture. They provide an environmentally friendly and more cost-effective solution compared to traditional solvents, as well as a more energy-efficient regeneration process.

In recent years, the field of solvent design and development has witnessed a growing interest in the exploration of deep eutectic solvents (DES) as environmentally friendly alternatives to conventional organic solvents.

Deep eutectic solvents (DES) have been widely recognised as a new class of compounds very similar to ionic liquids (ILs) due to their shared characteristics and properties. These extraordinary DES consist of a eutectic mixture of Lewis or Brønsted acids and bases, within which anionic and/or cationic species can be found. They are solvent systems created by combining two or more distinct components, each of which plays a well-defined role: one acts as a hydrogen-bond donor and the other as a hydrogen-bond acceptor. These components join by self-association, creating a eutectic mixture with a melting temperature substantially lower than that of its individual components.

DES are commonly regarded as next-generation ionic liquids due to several advantages such as:

- Excellent CO_2 absorption
- Wide liquid range
- Relatively low cost and high purity
- They can be made from 'green' and biodegradable materials.
- Low vapour pression.

Within the realm of deep eutectic solvents, one class that has distinctly risen to prominence is the imidazole-based deep eutectic solvents, owing to their versatile character and wide array of applications. Imidazole, a five-membered aromatic heterocyclic compound, assumes the role of a hydrogen bond acceptor within these DES systems, forging robust interactions with a myriad of hydrogen bond donors, including carboxylic acids, amines, alcohols, and metal salts. This remarkable versatility allows imidazole-based deep eutectic solvents to manifest an extensive range of physicochemical properties, permitting their tailoring to suit specific applications.

The exceptional attributes of imidazole-based deep eutectic solvents render them especially appealing for a multitude of industrial applications, encompassing catalysis, extraction, electrochemistry, and biomass conversion. These solvents have undergone exhaustive exploration as reaction media for diverse chemical transformations, such as organic synthesis, biocatalysis, and enzymatic reactions, thanks to their remarkable solvation capabilities and compatibility with a broad spectrum of substrates. Furthermore, their tuneable properties, including viscosity, polarity, and acidity, offer the precision required to fine-tune reaction conditions and selectivity, rendering them invaluable tools in the realm of chemistry and industrial processes. Moreover, imidazole-based deep eutectic solvents have demonstrated substantial promise as environmentally friendly solvents for the extraction and separation of diverse compounds derived from natural sources, including plants and biomass. Employing these solvents in extraction processes presents a host of advantages when compared to conventional organic solvents. These advantages encompass reduced toxicity, heightened selectivity, and an overall enhancement of sustainability. Additionally, their capacity to dissolve both polar and nonpolar compounds position them as exceptionally well-suited candidates for intricate sample matrices, further underlining their suitability for green and efficient extraction methodologies.

1.1.4 Type of DES

DESs could be defined as a general formula $R_1R_2R_3R_4N^+X^-Y^-$, and they can be divided into four types.

The classification of DES can be based on the type of components used in their formation. These can be divided as follows:

1. *Type 1: DES Formed by Metal Salts*

   In this category, the deep eutectic solvents are composed of metal salts as one of the primary components. Metal salts, such as choline chloride (a quaternary ammonium salt), are combined with other suitable compounds to create a eutectic mixture.

2. *Type 2: DES Formed by Hydrated Metal Salts*

   This type involves the use of hydrated metal salts in the formulation of deep eutectic solvents. The inclusion of water molecules in the metal salt structure contributes to the eutectic properties. The hydrated metal salts, combined with other components, result in deep eutectic solvents with specific characteristics, such as lower melting points and tunable properties.

3. *Type 3: DES Formed by Hydrogen Bond Donors from Organic Salt*
   Deep eutectic solvents are created by combining organic salts that serve as hydrogen bond donors. These organic salts can include compounds with functional groups capable of forming hydrogen bonds, such as urea derivatives. When these organic salts are paired with appropriate counterparts, eutectic mixtures with unique properties are formed.

4. *Type 4: DES Formed by Metal Salt Coupled with Alcohol or Amine*
   This type involves the combination of metal salts with alcohol or amine compounds (MClχ + RZ; M=Al, Zn; Z=CONH2, OH). The interaction between the metal salt and the alcohol or amine results in the formation of a eutectic mixture. These solvents may exhibit characteristics suitable for specific applications, and their properties can be adjusted by varying the ratio of the components.

Among the four types of DES, Type III DES is the most attractive to researchers, which is typically formed through hydrogen bond, where the charge delocalization occurring through hydrogen bonds between the halide anions and the HBDs leads to the decrease in the freezing point of the mixture. The photos below show the Illustration of Type III deep eutectic solvent with hydrogen bond formed and the eutectic graphic.

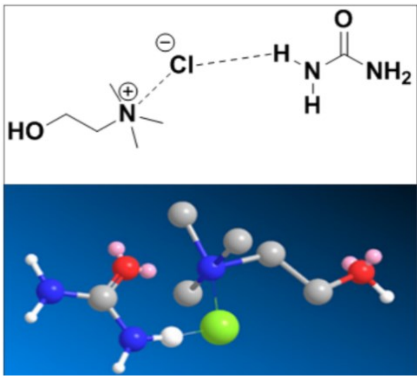


Figure 1.1: Illustration of Type III deep eutectic solvent with hydrogen bond formed [1]

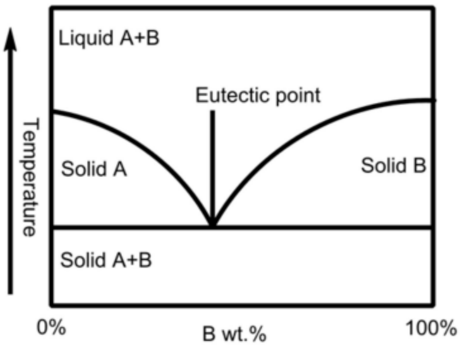


Figure 1.2: Principles behind Type III DES [2]

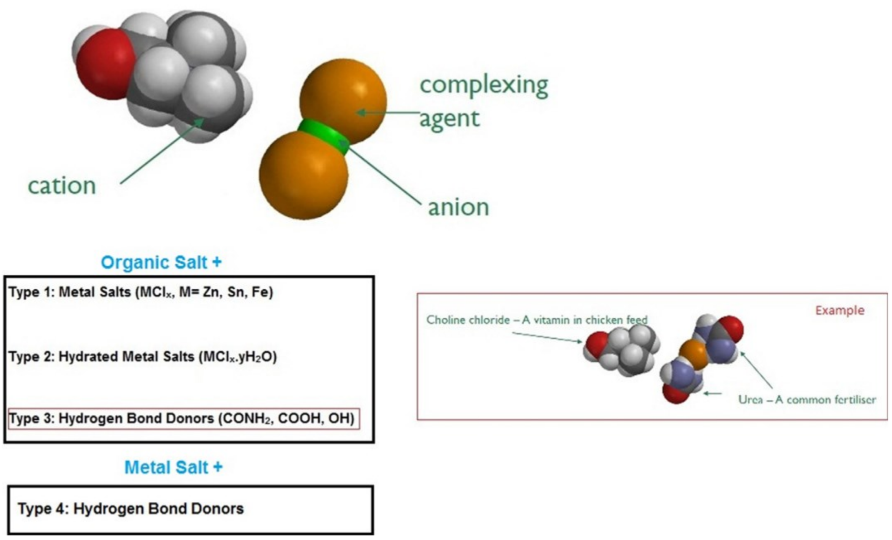


Figure 1.3: Types of deep eutectic solvents (DESs) and one example of a eutectic mixture between choline chloride and urea.[3]

1.1.5 Study on DES

The initial iteration of Deep Eutectic Solvent (DES) was introduced by Abbott and colleagues [4]. It consisted of a mixture of choline chloride (ChCl) and urea in a 1:2 molar ratio. It's worth noting that both these constituents are non-harmful, readily accessible and biodegradable.

For the very first time, Li and his team conducted a study examining the solubility of CO_2 in eutectic combinations of ChCl and urea at molar ratios of 1:1.5, 1:2, 1:2.5, taking into account variations in pressure (up to 13 MPa) and temperature (313.15, 323.15 and 333.15 K).[5]

Their research findings unveiled that the solubility of CO_2 in Deep Eutectic Solvents (DESs) hinged on factors such as the ratio of salt to hydrogen bond donor (HBD), as well as the prevailing pressure and temperature conditions. As pressure increased and temperature decreased, the solubility of CO_2 saw a corresponding rise. Within the spectrum of DESs they scrutinized, Choline Chloride (ChCl) and urea at a 1:2 molar ratio exhibited the most substantial CO_2 solubility. In comparison, CO_2 solubilities in these studied DESs followed a similar trend to that of ammonium-based ionic liquids (ILs) but are lower than those of imidazolium-based ILs when subjected to comparable conditions.

The choice of the hydrogen bond donor (HBD) significantly influences CO_2 solubility in DESs. For instance, when lactic acid serves as the HBD, the CO_2 absorption capacity is less than that of urea based DESs with the same 1:2 molar ratio [6]. Conversely, deploying glycerol or ethylene glycol as the HBD enhances CO_2 absorption capacity to match that of imidazolium based ILs [7, 8]. All these DESs have the ability to physically absorb CO_2.

Sze and colleagues reported the pioneering of a task-specific Des system, comprising ChCl, Glycerol and a superbase (the term superbase denotes an extremely strong base that practically succeeds in stripping H+ ions from almost all known compounds) [9].

The superbase played a crucial role in deprotonating the OH groups in glycerol and ChCl, leading to the creation of active alkoxide anions. These active species enabled the reversible capture of CO_2

under ambient conditions. Nevertheless, in comparison to traditional ILs, researches on DESs as CO_2 sorbents remains somewhat limited, and the CO_2 absorption capacities of available DESs sill appear relatively modest.

Ghaedi and colleagues reported their findings on CO_2 solubility in Deep Eutectic Solvents (DESs), specifically in allylthiphenyl phosponium bromide-diethylene glycol and allyltriphenyl phosphonium bromide-triethylene gycol systems, at a pressure up to 2 MPa and a temperature of 303.15 K.

Their research demonstrated that the CO_2 solubility in DESs based on triethylene glycol surpassed that of diethylene glycol based DESs, primarily due to a greater available free volume and molar volume. Additionally, the enhanced CO_2 solubility in the former DES can be attributed to the additional ethylene and ether groups present. [10]

In a separate study Zhang and their team examined the solubility of CO_2 in task specific DESs. Which were composed of 1-butyl-3-methylimidazolium chloride and imidazole in varying molar ratios, with the inclusion of 1,5-diazabicyclo [4.3.0] non-5-ene (DBN) superbase as a task-specific agent. They conducted in-situ infrared analysis to scrutinize the gas absorption process. While the absorption mechanism was proposed by merging experimental results with Nuclear Magnetic Resonance (NMR) analysis and Density Functional Theory (DFT) calculations. The DESs under investigation exhibited commendable thermal stability and reusability, coupled with a notable absorption capacity of 1.07 mol_{CO2}/mol_{DES} at 25 °C and I bar [11]

Figure below reported summarizes the chemical structures along with their molar ratios for the most common DESs in the literature.

The table 2.1 shows absorption values found in the literature, which reflect the constant research employed in this particular field.

Table 1.1: Absorption values for different studies

Study	DES	Absorption Value
Kai Zhang et All. [28]	[TETA]·Cl-EG	1.46 mol_{CO2}/mol_{DES}
Kai Zhang et All. [28]	[ChCl]-urea (7:1)	0.92 mol_{CO2}/mol_{DES}
Jiang et All. [29]	DBN-2-imidazolidone (2-1)	1.75 mol_{CO2}/mol_{DES}
Shokat et All. [30]	MTPP–AC (1:4)	3.22 mol_{CO2}/Kg_{DES}

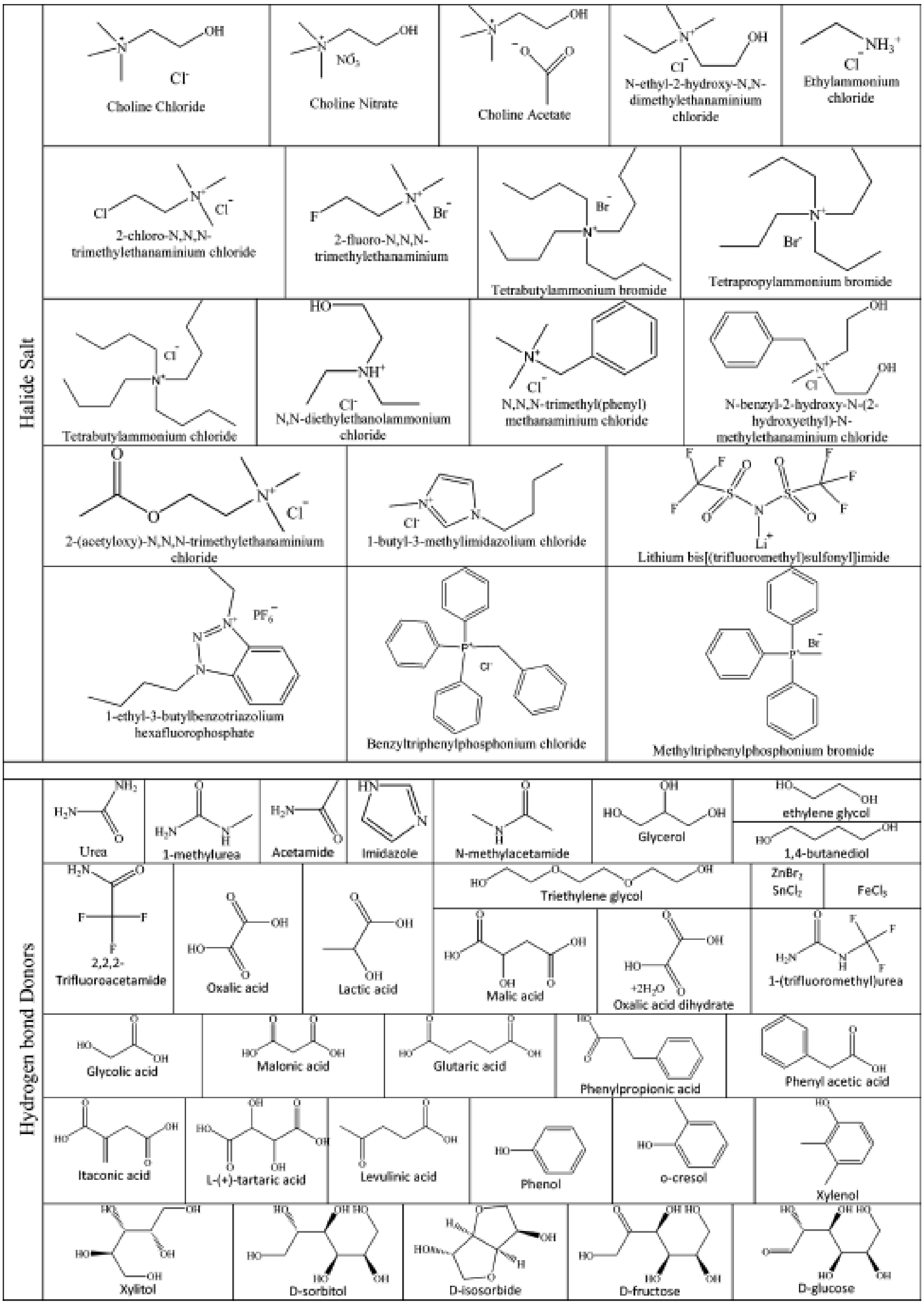


Figure 1.4: Most common structures of hydrogen-bond donors and halide salts used in the preparation of DESs.[12]

1.1.6 CO_2 absorption measurements

The experimental apparatus designed for the chemical and physical absorption of carbon dioxide (CO_2) is described in detail in the following passage. Within a meticulously controlled environment, namely a sealed tank filled with high-purity distilled water and maintained at a constant temperature of 25 degrees Celsius, an intricate system has been devised to facilitate the absorption of CO_2. This system comprises several key components that work in concert to ensure precision and reproducibility in the CO_2 absorption process.

At the heart of this setup is a reservoir, meticulously engineered with precise dimensions and a known volume, into which CO_2 is introduced directly from the primary gas cylinder. This reservoir is intrinsically linked via a valve to a reactor, similarly, characterized by exact volume and geometry specifications. Within this reactor, a magnetic stirring bar, also of defined volume and geometry, is suspended. The reactor houses a deep eutectic solvent (DES), meticulously prepared and primed for CO_2 capture.

The experimental procedure commences with the introduction of a precisely measured volume of DES, typically ranging from 2 to 3 millilitres, into the reactor. Subsequently, the reactor is securely connected to the tubing system that links the reservoir, the valve, and the reactor itself. The entire system is allowed to equilibrate within a temperature-controlled chamber until it reaches the desired operating temperature of 25 degrees Celsius, a process typically requiring approximately 20 to 30 minutes. This chamber is equipped with a sophisticated temperature control system that enables precise adjustment of the bath temperature to the specified setpoint.

For visual clarity and reference, the diagram provided below illustrates the CO_2 capture setup in its entirety, offering a comprehensive view of the experimental apparatus.

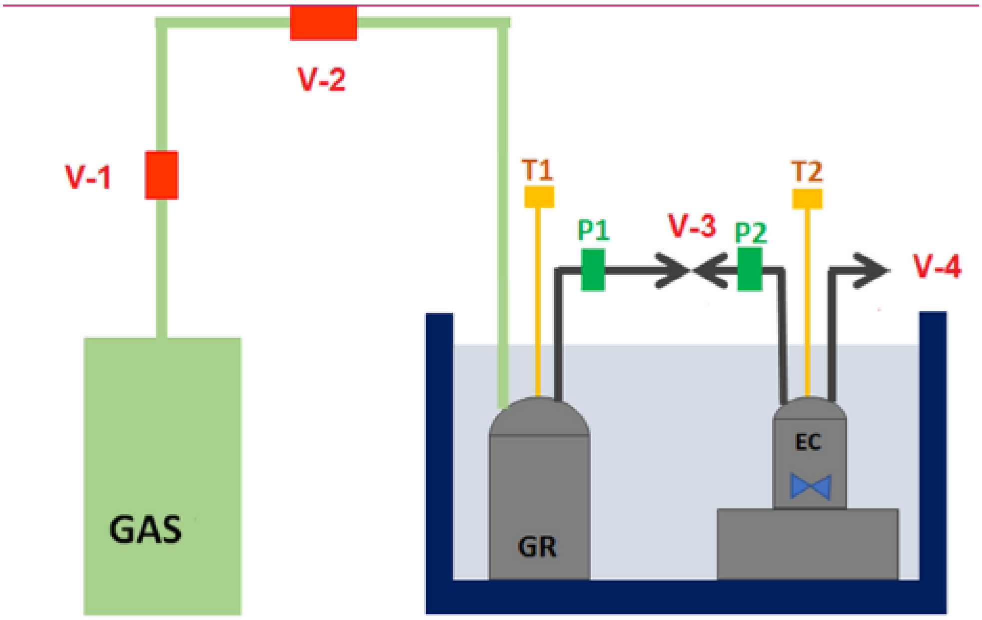


Figure 1.5: Set-Up for CO_2 absorption into DES

In the endeavour to ascertain the quantity of carbon dioxide (CO_2) that has been effectively captured within of our experimental setup, we have turned to the fundamental precepts enshrined within the ideal gas law, which entails the formulation of equations to describe the behaviour of CO_2 within both the equilibrium cell and the reservoir.

The application of the ideal gas law is pivotal for our pursuit of precisely quantifying the CO_2 captured, affording us the mathematical framework to vividly represent and comprehend the myriad processes unfolding within our experimental setup. It provides us with the means to extract tangible and precise knowledge about what happens to CO_2 when it comes in contact with the deep eutectic solvent and its surroundings in a highly controlled environment.

In the subsequent sections, we will present these equations in a formal mathematical notation to provide a rigorous and quantitative understanding of the carbon dioxide capture process.

To elucidate this concept further, we express these equations as follows:

1) *Equation for the Equilibrium Cell:*

In the context of the equilibrium cell, where CO_2 is in direct interaction with the deep eutectic solvent (DES), we employ the ideal gas law, expressed as:

$$P_{ec}V_{ec} = n_{ec}RT. \tag{1.1}$$

Where:

- $P_{ec} = Pressure\ of\ CO_2\ in\ the\ equilibrium\ cell\ [MPa]$
- $V_{eq} = Volume\ of\ the\ equilibrium\ cell\ [cm^3]$, in which we have to subtract the volume of the DES (3 ml)
- $n_{eq} = mole\ of\ CO_2\ in\ the\ equilibrium\ cell\ [mol]$
- $R = Gas\ Constant\ \left(0.000008314\left[\frac{m^3 MPa}{K*mol}\right]\right)$
- $T = Absolute\ Temperature\ of\ the\ set\ up\ (298\ K)$

2) *Equation for the Reservoir:*

In the reservoir, the behaviour of CO_2 is also governed by the ideal gas law, which is articulated as:

$$P_rV_r = n_rRT. \tag{1.2}$$

In this equation:

- $P_r = Pressure\ of\ CO_2\ in\ the\ reservoi\ [MPa]$
- $V_r = Volume\ of\ the\ Reservoir\ [cm^3]$
- $n_r = mole\ of\ CO_2\ in\ the\ reservoir\ [mol]$

- $R = Gas\ Constant\ \left(0.000008314 \left[\frac{m^3 MPa}{K*mol}\right]\right)$
- $T = Absolute\ Temperature\ of\ the\ set\ up\ (298\ K)$

Following the absorption of carbon dioxide (CO_2) into the absorption cell, a discernible trend emerged wherein the pressure within the cell exhibited a gradual growth.

After a period of time, the pressure ultimately levelled off and remained constant. This plateaued pressure level, once reached, served as an indicative point where it was reasonably postulated that the system had attained a state of equilibrium, characterized by the dynamic equilibrium between the CO_2 dissolved in the deep eutectic solvent (DES) and that present in the vapor phase.

To ascertain the equilibrium state with precision, the pressure at this stabilized point was carefully monitored and recorded for subsequent analysis. Underpinning this assumption was the consideration that the vapor phase predominantly consisted of pure CO_2, owing to the notably negligible vapor pressure exhibited by the deep eutectic solvents employed in the process. This assumption allowed for the application of the previously mentioned equations derived from the ideal gas law to calculate the number of moles of CO_2 that had become dissolved within the DES.

In order to provide a reliable estimation of the accuracy of the solubility values, an assessment of the overall uncertainty was undertaken, and it was found to be within a range of ±0.001.

1.2 CONVERSION

1.2.1 Why the conversion of CO_2

Electroreduction, also known as electrochemical reduction, is a process in which electric current is used to drive a chemical reaction that results in the reduction (gain of electrons) of a chemical species. This reduction reaction typically involves the transfer of electrons to a substance, causing it to undergo a change in its oxidation state or chemical structure. Electroreduction is a fundamental concept in electrochemistry and plays a significant role in various applications, including industrial processes, energy storage, and environmental remediation.

Carbon dioxide (CO_2) electroreduction has emerged as an innovative technology with the potential to simultaneously address two pressing global challenges:

1. climate change.
2. sustainable energy production.

Among the various approaches developed to harness CO_2 as a raw material for valuable chemical compounds and renewable energy, the use of deep eutectic solvents (DES) has garnered considerable attention. Deep eutectic solvents, a class of environmentally friendly and inexpensive ionic liquids, offer a versatile means of electrochemically reducing CO_2, opening up a myriad of possibilities for mitigating greenhouse gas emissions and producing valuable products. This innovative approach has the potential to revolutionise our efforts to combat climate change and transition to a more sustainable, zero-emission future.

Electrochemical CO_2 reduction (ECO_2R) is one of the most viable and economical methods to store renewable energy by producing sustainable fuels (e.g., formic acid for fuel cell applications), feedstock chemicals (e.g., syngas), commodity chemicals (e.g., methane), intermediates (e.g., oxalate) and task specific products.

The applications of deep eutectic solvents as electrolytes in CO_2 electroreductions has sown promising results in the generation of various chemical products, including formate, carbon monoxide, methane, ethylene, and ethanol.

1.2.2 Study on DES for the conversion of CO_2

In recent years, there has been a growing interest in the field of carbon capture and utilization (CCU), which involves the conversion of carbon dioxide into fuels and chemicals. This process utilizes amine solutions as electrolytes in the electrochemical reduction of CO_2. [13, 14]

Abdinejad and colleagues conducted research using ethylene diamine (EDA) in an aqueous $NaClO_4$ solution and achieved a 58% Faradaic efficiency for carbon monoxide (FECO) at the copper surface [15].

Meanwhile, Chen and their team employed a 30% aqueous monoethanolamine (MEA) solution as an electrolyte [10]. Among eight different metallic catalysts tested, only silver (Ag) displayed a 39.1%

faradaic efficiency for CO production, while indium (In) exhibited a 45% faradaic efficiency for formate ions (FEHCOO) [14].

Notably, the CO_2 molecules approached the electrode primarily as free CO_2 species in the electrolyte rather than CO_2-rich carbamate species. As a result, a significant portion of the captured CO_2 remained unused.

Chen and colleagues proposed that enhancing CO generation could be achieved by using electrolytes that form a weak bond between CO_2 and the amine molecules [14].

The choice of deep eutectic solvent composition, the selection of appropriate electrocatalyst, and the optimization of reaction parameters play crucial role in achieving high selectivity and efficiency in CO_2 conversion.

Lately, an examination conducted by Paul and his colleagues [16] succinctly outlined the progressions in electrochemical transformation of carbon dioxide into value-enhancing chemicals through electroreduction. The article also delves into noteworthy advancements in identifying less harmful deep eutectic solvents (DESs) for scaling up the technology of CO_2 electroconversion and portraying it as a sustainable process.

Similar study was carried out by Jonathan Albo et all [18], in which an attempt was made to produce methanol from carbon dioxide.

Nonetheless, the comprehension of the mechanistic intricacies surrounding CO_2 capture and electrochemical conversion within DES remains somewhat elusive.

So, there is a need to make new electrolytes to modulate CO_2 reduction via CO_2 adsorption.

The electrochemical reduction of CO_2 in the presence of deep eutectic solvents offers several advantages over conventional electrolyte systems. Firstly, deep eutectic solvents can provide a favourable electrolyte environment for CO_2 activation and subsequent reactions. The unique solvation properties of DES can enhance the solubility of CO_2 and stabilize reactive intermediates, thereby improving the selectivity and efficiency of the electrochemical process.

Deep eutectic solvents can play a dual role by acting as both electrolyte and reaction media. Their ability to dissolve various reactants and catalysts can facilitate the mass transfer of reactants to the electrode surface, ensuring efficient electrocatalysis and promoting desirable reaction pathways.

The tuneable nature of deep eutectic solvents allows for the optimization of the solvent composition to tailor the reaction conditions and selectivity, enabling the production of a wide range of value-added chemicals from CO_2.

As part of our research, we undertook a comprehensive exploration of the conversion characteristics of Im-MEA (1:2), a compound that has attracted a great deal of attention for its remarkable CO_2 absorption capabilities. In particular, Im-MEA's performance in this respect is second only to Im-DEA (1:2).

The experimental apparatus specifically crafted for this investigation is illustrated in the image provided below. This setup played a pivotal role in enabling a methodical and comprehensive examination of the CO_2 reduction properties harnessed by Deep Eutectic Solvents (DES).

1.2.3 Experimental Set-Up

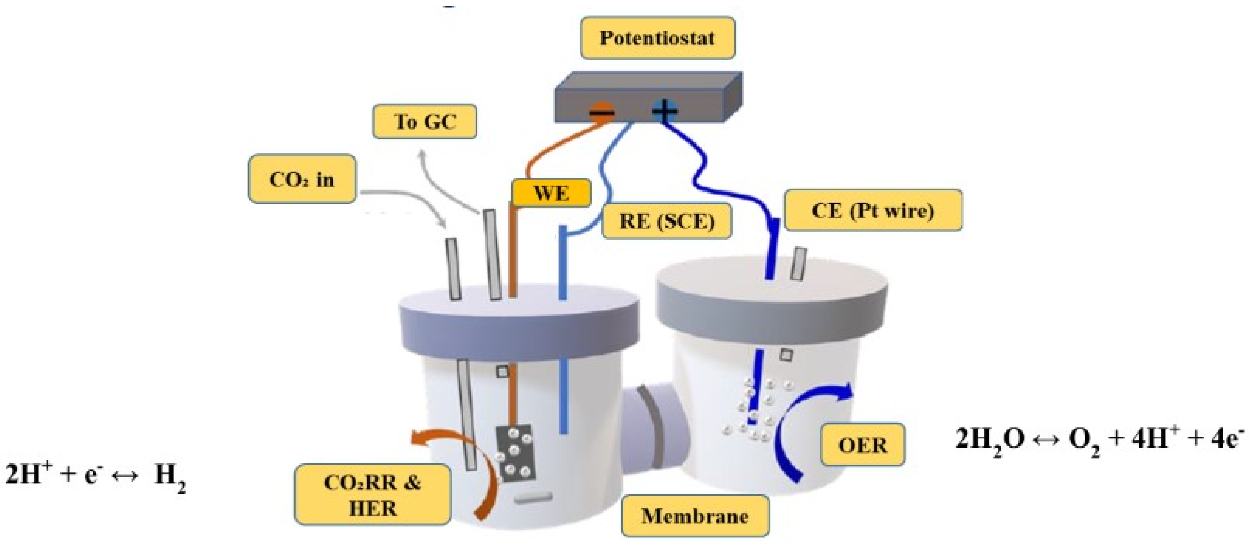


Figure 1.6: Experimental Set-Up for the electroreduction

This system comprises two distinct components: one contains the positively charged cation electrode and the other the negatively charged anion electrode. These electrodes are seamlessly connected to a potentiostat, which is the essential hardware apparatus for adjusting a three-electrode cell and performing a wide range of electroanalytical experiments.

Electrochemical assessments were conducted within a specialized experimental setup, specifically a three-electrode system consisting of two separate chambers in an H-shaped electrolytic cell. These experiments were carried out by utilizing a state-of-the-art electrochemical workstation known as the "Solartron Analytical electrochemical workstation." In this setup, the counter electrode employed was composed of platinum (Pt) sheet material, while the reference electrode utilized was of the Ag/AgCl type. A carbon paper electrode with N-CND, characterized by its geometric area measuring approximately 0.5 square centimeters by 2.0 square centimeters, was employed as the working electrode in this experimental setup. Within the H-type electrolytic cell, the two compartments were discreetly partitioned by means of a proton exchange membrane, specifically the Nafion 117 proton exchange membrane, which was sourced from Sigma–Aldrich. The primary function of this membrane was to act as a barrier, effectively preventing the undesired reoxidation of the reduction products situated within the cathode compartment.

A 0.1 molar (M) concentration of Deep Eutectic Solvent (DES) solution served as the electrolytic medium in this experiment. To create the electrolytic environment, a total volume of 10 millilitres (mL) of the electrolyte solution was meticulously introduced into each of the respective compartments within the experimental setup. Prior to each electrochemical test, the electrolyte solution underwent a saturation process with carbon dioxide (CO2). This saturation was achieved by continuously passing CO2 gas through the solution at a controlled flow rate of 10 mL per minute for a duration of no less than 30 minutes. The CO_2 reduction performed at –1.2 V (vs Ag/AgCl) and the CO products formed with the time of 3600 seconds.

CHAPTER 2

EXPERIMENTAL PART

In this chapter, all procedures employed for undertaking this study are accurately elucidated. The initial section pertains to the chemicals utilized in various experiments and details all analytical instruments employed in this study. Subsequently, the formation of electrodes for electroconvection is explained, followed by the description of the thermodynamic model utilized and an explanation of how critical properties were calculated.

2.1 Chemicals for the creation of DESs

The formulation of deep eutectic solvents is based on a specific selection of chemical components, which are carefully curated to achieve the desired properties and characteristics. The list of key chemicals used in the synthesis of these deep eutectic solvents is elaborated below, complete with their purity and reference sources:

2.1.1 Monoethanolamine (MEA):

It's a versatile organic compound, is a colourless, viscous liquid with a faint odor. Its chemical formula is C_2H_7NO, and it is classified as both an amine and an alcohol due to its unique chemical structure. MEA has a wide range of applications and is primarily known for its role in the chemical, pharmaceutical, and petrochemical industries.

Sourced from the Aldrich company, this component boasts a purity of 99.9 per cent. MEA is a key element in the creation of deep eutectic solvents, known for its ability to form hydrogen bonds and contribute to unique solvent properties. Some of the properties are presented below and the chemical structure is shown in figure 2.1:

- Molecular Weight: 61.084 g/mol
- Melting Point: 283.4 K
- Boiling Point: 443 K
- Density (@25°C): 1.0117 g/cm3
- Viscosity (@25°C): 43 cP

Figure 2.1: Monoethanolamine Molecule

2.1.2 *Diethylamine (DEA):*

Diethylamine, often abbreviated as DEA, is a chemical compound that belongs to the family of amines. It is a versatile organic compound with a range of industrial and laboratory applications. Diethylamine has the chemical formula $C_4H_{11}N$ and is classified as a secondary amine. Its structure consists of two ethyl groups (C_2H_5) attached to a central nitrogen atom, which makes it an aliphatic secondary amine. It is a colorless and highly flammable liquid at room temperature. It has a strong, ammonia-like odor and is miscible with water, as well as many organic solvents.

Also from Aldrich, DEA offers a remarkable purity of 99.5%. It plays a significant role in the formation of deep eutectic solvents, contributing to their chemical reactivity and solubility.

Some of the properties are presented below and the chemical structure is shown in figure 2.2:

- Molecular Weight: 73.14 g/mol
- Melting Point: 223.35 K
- Boiling Point: 239.55 K
- Density (@25°C): 0.706 g/cm3
- Viscosity (@25°C): 0.336 cP

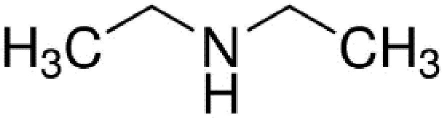


Figure 2.2: Diethyliamine Molecule

2.1.3 *Pentaethylenehexamine (PEHA):*

Pentaethylenehexamine, often abbreviated as PEHA, is a chemical compound that belongs to the class of polyamines. It consists of a linear chain of six ethylene (C_2H_4) units, connected by five nitrogen atoms. This arrangement gives it its characteristic properties.

Pentaethylenehexamine (PEHA) is typically a colourless or pale-yellow liquid. Its colour can vary depending on factors such as purity and exposure to environmental conditions.

This component, also from Aldrich, maintains a high level of purity of 99.9%. PEHA is fundamental for the creation of deep eutectic solvents, influencing their acidity and basicity, which in turn affects their solvation capacity.

Some of the properties are presented below and the chemical structure is shown in figure 2.3:

- Molecular Weight: 328.58 g/mol
- Melting Point: 310.15 K
- Boiling Point: 412 K
- Density (@25°C): 1.003 g/cm3

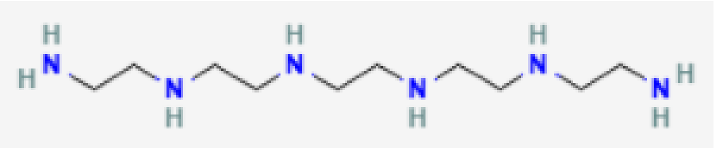


Figure 2.3: PEHA Molecule

2.1.4 *Tetrapropylammonium bromide (TPAB):*

Tetrapropylammonium bromide, often abbreviated as TPrAB or TPAB, is a chemical compound belonging to the family of quaternary ammonium salts. It consists of a central nitrogen atom (N) bonded to four propyl groups (C_3H_7) and a bromine ion (Br-). The nitrogen atom carries a positive charge, resulting in a quaternary ammonium ion structure. Tetrapropylammonium bromide is typically a white crystalline solid at room temperature. It is sparingly soluble in water but can dissolve in various organic solvents.

With a purity level of 99%, Aldrich's TPAB is a key component in the formulation of deep eutectic solvents. It imparts unique properties to the resulting solvents, including ionic conductivity and stability.

Some of the properties are presented below and the chemical structure is shown in figure 2.4:

- Molecular Weight: 259.15 g/mol
- Melting Point: 492.15 K
- Boiling Point: //
- Density (@25°C): 1.18 g/cm3

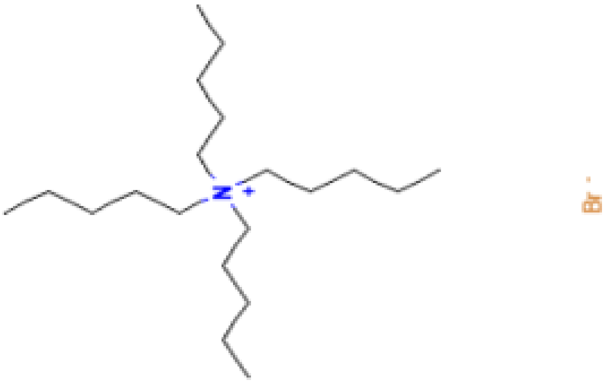


Figure 2.4: TPAB Molecule

2.1.5 *Acetic acid:*

Acetic acid, also known as ethanoic acid, is a well know organic acid. The chemical formula of acetic acid is CH_3COOH, which represents its molecular structure. It consists of two carbon atoms, four hydrogen atoms, and two oxygen atoms. The carboxyl group (-COOH) is responsible for its acidic properties.

Acetic acid is a colourless, pungent-smelling liquid at room temperature.

An essential organic acid, acetic acid contributes to the overall chemical composition of deep eutectic solvents, influencing their acidity and reactivity.

Some of the properties are presented below and the chemical structure is shown in figure 2.5:

- Molecular Weight: 60.05 g/mol
- Melting Point: 289.75 K
- Boiling Point: 391.25 K
- Density (@25°C): 1.049 g/cm3
- Viscosity (@25°C): 1.22 cP

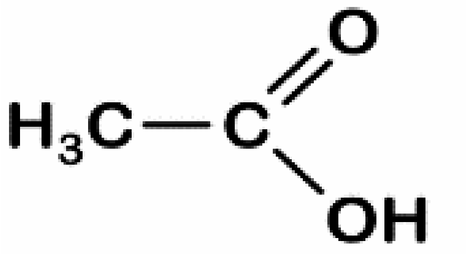


Figure 2.5: Acetic Acid Molecule

2.1.6 Formic acid:

Formic acid, with the chemical formula HCOOH, is a simple and fascinating organic compound. It consists of a carboxyl group (-COOH) attached to a single hydrogen atom. This arrangement makes it one of the simplest organic acids. Formic acid is a colourless liquid. It is transparent and does not exhibit any inherent colour, which is typical for many organic compounds in their pure form.

Formic acid plays a central role in the chemical composition of these solvents, contributing to their overall characteristics.

A presentation of select properties is provided below, with Figure 2.6 depicting the chemical structure.

- Molecular Weight: 46.03 g/mol
- Melting Point: 281.55 K
- Boiling Point: 373.95 K
- Density (@25°C): 1.22 g/cm3
- Viscosity (@25°C): 1.8 cP

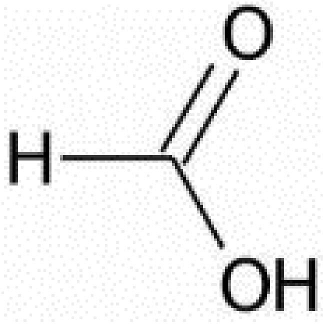


Figure 2.6: Formic Acid Molecule

2.1.7 Imidazole:

It is a five-membered heterocyclic ring containing two nitrogen atoms at positions 1 and 3, and it is chemically classified as an aromatic compound. The presence of two nitrogen atoms within the ring makes it an important functional group in many biochemical and pharmaceutical compounds. Imidazole is typically a white or colourless crystalline solid. In its pure form, it does not possess any inherent colour. However, the appearance of imidazole can vary depending on its specific form (e.g., as a powder or crystals) and any impurities it might contain.

Imidazole is used in the creation of deep eutectic solvents, where it contributes to their ionic character and enhances their unique properties.

A presentation of select properties is provided below, with Figure 2.7 depicting the chemical structure.

- Molecular Weight: 68.08 g/mol
- Melting Point: 363.15 K
- Boiling Point: 529 K
- Density (@25°C): 1.23 g/cm3

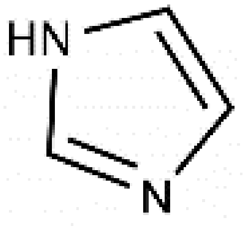


Figure 2.7: Imidazole Molecule

2.1.8 CO_2:

Carbon dioxide (CO_2) is a colourless, odourless gas that plays a significant role in our planet's atmosphere and is a topic of growing concern due to its impact on climate change.

it is used to study the chemical and physical adsorption phenomena within the deep eutectic solvents created.

A presentation of select properties is provided below, with Figure 2.8 depicting the chemical structure.

- Molecular Weight: 44.01 g/mol
- Melting Point: 194.65 K
- Boiling Point: 194.65 K (It transitions directly from a gas to a solid)
- Density (@25°C): 1.84 g/cm3
- Viscosity (@25°C): 0.067 cP

Figure 2.8: Carbon Dioxide Molecule

All the chemicals mentioned above have been used in their analytical grade, without the need for further purification. This emphasises the care and precision in the selection of these chemicals, as their high purity and quality are crucial to ensure the desired characteristics of the resulting deep eutectic solvents.

2.2 Chemicals for the electroreduction part

2.2.1 Platinum sheet material

Platinum sheet material is a highly prized and versatile substance in the field of electrode fabrication. Its unique properties make it an excellent choice for various electrochemical applications, ranging from fuel cells to electroplating processes. Platinum is renowned for its exceptional resistance to corrosion, even in aggressive chemical environments. This property ensures that platinum electrodes maintain their structural integrity and functionality over extended periods, making them suitable for long-term use.

Platinum has a stable and relatively low electrode potential and is an outstanding catalyst, which is essential for many electrochemical processes. The photo below shows the electrode used in our study.

Figure 2.10: Platinum Sheet Electrode

2.2.2 Nafion 117 proton exchange membrane.

Nafion 117 is a perfluoro sulfonic acid ionomer, belonging to the Nafion family of materials. It is composed of a fluorocarbon backbone with pendant sulfonic acid groups. This particolar chemical structure imparts several important properties to Nafion 117, making it an ideal material for PEM applications. The perfluorinated backbone provides the material with excellent chemical resistance, while the sulfonic acid groups facilitate proton conduction. In the subsequent investigation, commercially acquired membranes were employed in the electrolytic cell.

It's a proton exchange membrane that has significantly influenced the field of electrochemical energy conversion, particularly in the realm of fuel cells. Its unique properties, including high proton conductivity, water uptake capacity, chemical and thermal stability, and mechanical durability, make it an indispensable material for various applications in the pursuit of clean and sustainable energy.

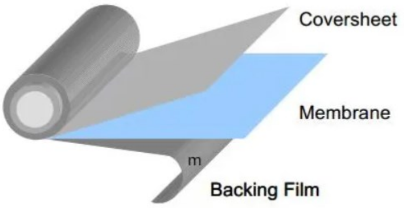


Figure 2.11: Nafion 117 Structure

2.2.3 Ethanol

Ethanol, also known as ethyl alcohol, is a colourless, flammable, and volatile chemical compound with the chemical formula C_2H_5OH. It is one of the most widely used and important organic compounds in the world. Ethanol has a long and varied history of human use, serving as both a recreational beverage and an essential industrial and fuel component.

A presentation of select properties is provided below, with Figure 2 depicting the chemical structure.

- Molecular Weight: 46.07 g/mol
- Melting Point: 159 K
- Boiling Point: 351.52 K
- Density (@25°C): 0.789 g/cm3
- Viscosity (@25°C): 1.074 cP

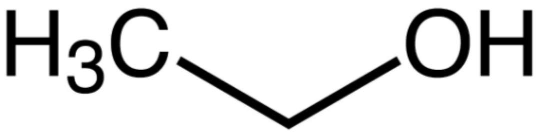


Figure 2.12: Ethanol Molecule

2.2.4 *Phosphoric Acid (anhydrous):*

Phosphoric acid, with the chemical formula H_3PO_4, is a mineral and inorganic acid that plays a vital role in various industrial, agricultural, and food-related applications. Phosphoric acid is a strong, colourless, doorless, and highly corrosive acid. It is a triprotic acid, meaning it can donate up to three protons (hydrogen ions) in aqueous solutions. Due to its corrosive nature, phosphoric acid must be handled with care. A presentation of select properties is provided below, with Figure 2 depicting the chemical structure.

- Molecular Weight: 97.99 g/mol
- Melting Point: 315.50 K
- Boiling Point: 485.15 K
- Density (@25°C): 1.685 g/cm3
- Viscosity (@25°C): 147 cP

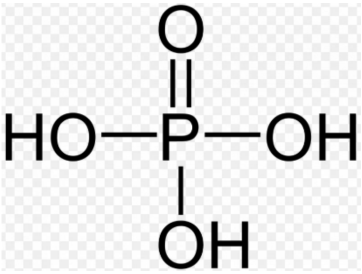


Figure 2.13: Phosphoric Acid Molecule

2.3 DES preparation

The study I conducted involved a comprehensive investigation into the preparation and subsequent characterisation of six distinct deep eutectic solvents (DES) designed specifically for CO_2 capture applications. In this research, a clear distinction was made between two categories of DES: those associated with chemical adsorption and those associated with physical adsorption.

The initial phase of the study focused on the preparation of these DESs. This process involved the mixing of a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD), and the mixture was maintained at a constant temperature of 50 degrees Celsius for an appropriate period of time. This time frame typically ranged from 30 minutes to half an hour, ensuring the formation of a well-defined mixture. Once the DES formulation was complete, it was gently cooled to room temperature.

It is worth noting that all the DES synthesised during this study exhibited a common property: they remained in a liquid state at room temperature and possessed melting points below 25 degrees Celsius. This characteristic is crucial for their usefulness in CO_2 capture applications.

Furthermore, after the steps described above, the DES preparations were deemed ready for immediate use without the need for further purification. This emphasises the precision and care employed in the preparation process, ensuring that the DES were of high quality and purity. To maintain their integrity, the synthesised DES were safely sealed in vials and stored at room temperature, preserving their unique properties.

For a complete overview of the deep eutectic solvents prepared, two tables are presented (Table 1 and Table 2) that provide an overview of their individual compositions and characteristics. The tables presented below are unequivocally distinct: one is dedicated to deep eutectic solvents (DES), created specifically for chemical absorption of CO_2, while the other is designed exclusively for physical absorption of CO_2. The next section will delineate the differentiation between chemical and physical absorption.

Table 2.1: DES for chemical Absorption

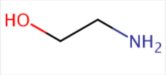
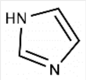
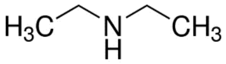
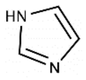
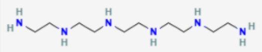
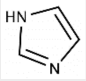
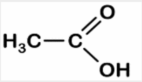
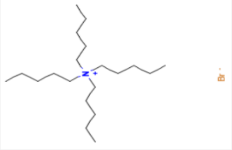
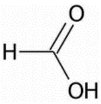
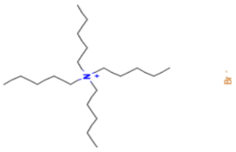
DES	***HBD***	***HBA***	***Molecular Structure of HBD***	***Molecular Structure of HBA***	***Weight Ratio***
Im-MEA	Monoethanolamine	Imidazole			(1:2)
Im-MEA	Monoethanolamine	Imidazole	\\	\\	(1:3)
Im-MEA	Monoethanolamine	Imidazole	\\	\\	(1:4)
Im-DEA	Diethylamine	Imidazole			(1:2)
Im-PEHA	Pentaethylenehexamine	Imidazole			(1:2)

Table 2.2: DES for physical absorption

DES	***HBD***	***HBA***	***Molecular Structure of HBD***	***Molecular Structure of HBA***	***Weight Ratio***
TPAB-Acetic Acid	Acetic Acid	Tetrapentylammonium bromide			(1:2)
TPAB-Formic Acid	Formic Acid	Tetrapentylammonium bromide			(1:2)

2.4 Synthesis of nitrogen rich carbon nano dots (N-CND)

In the dynamic landscape of advanced materials and energy-related research, Nitrogen-rich Carbon Nano Dots, abbreviated as N-CND, have emerged as a compelling class of nanomaterials with significant implications in electroreduction processes. These minuscule carbon-based nanoparticles, typically less than 10 nanometers in size, possess a unique blend of properties that make them integral to the development of efficient electrocatalysts and electrode materials for a wide range of electroreduction applications.

N-CNDs are a subset of carbon nanodots, characterized by their exceptional optical and electronic properties. What sets them apart is the substantial nitrogen content seamlessly incorporated into their carbon matrix, resulting in a fascinating interplay of elements that holds promise in the realm of electroreduction.

The N-doped porous carbon materials for our study were derived through a straightforward, single-step process involving the activation of nitrogen-enriched biomass precursors sourced from Fraction 3 of Spruce needles.

In a conventional synthesis procedure, 10 grams of biomass particles (Spruce Needles), with a particle size below 250 micrometres, were intimately combined with a 50% aqueous solution of phosphoric acid, employing a weight ratio of 1 part biomass to 2 parts phosphoric acid. This mixture was left to sit for 24 hours under regular environmental conditions.

Subsequently, the matured biomass samples were carefully transferred into ceramic crucibles and positioned inside a muffle furnace for the ensuing stages of the process.

Ultimately, the prepared samples underwent an activation process by subjecting them to a temperature of 500 degrees Celsius for a duration of 1 hour within a self-generated atmosphere. During this activation, the heating rate was meticulously maintained at 2.8 degrees Celsius per minute.

The outcome of this process was a series of doped carbon materials, which were then transformed into a powdered form, ensuring that the particle size remained below 100 micrometres.

These powders were subjected to a rigorous washing procedure using hot deionized water at a temperature of 90 degrees Celsius, which was continued until the pH level of the washed material reached a state of neutrality. Subsequently, the washed carbon powders were carefully dried in an oven set at a temperature of 100 degrees Celsius, allowing them to desiccate for a duration of 24 hours. These processed materials were then preserved for later use.

Within the activation procedure, phosphoric acid (H_3PO_4) serves a dual role, functioning also as a dehydrating agent. It has been observed that H_3PO_4 operates as an acid catalyst, thereby fostering the cleavage of chemical bonds and facilitating the establishment of crosslinks through dehydrative mechanisms, encompassing processes like cyclization and condensation.

The residual presence of the activating agent within the particles during the thermal treatment serves as a structural template for the genesis of microporous characteristics. Furthermore, phosphoric acid (H_3PO_4) has the capacity to engage with organic constituents, giving rise to the generation of phosphate and polyphosphate bridges. These bridges, in turn, serve to interconnect various fragments of the biopolymer, eliciting a network of chemical bonds.

The introduction of phosphate groups catalyzes a dilation process, leaving the matrix in an expanded state replete with an accessible pore architecture once the acid has been removed. As a result, the prepared Carbon Nano Dots (CND) materials are rendered capable of both donating and accepting electrons, endowing them with a distinctive reactivity. This unique quality also positions them as highly effective catalysts in a spectrum of other catalytic reactions.

The image below provides a comprehensive visual representation of the process employed for the generation of the Carbon Nano Dots (CNDs) utilized in this research. The visual representation of the nanodots will be provided in the commentary and results section.

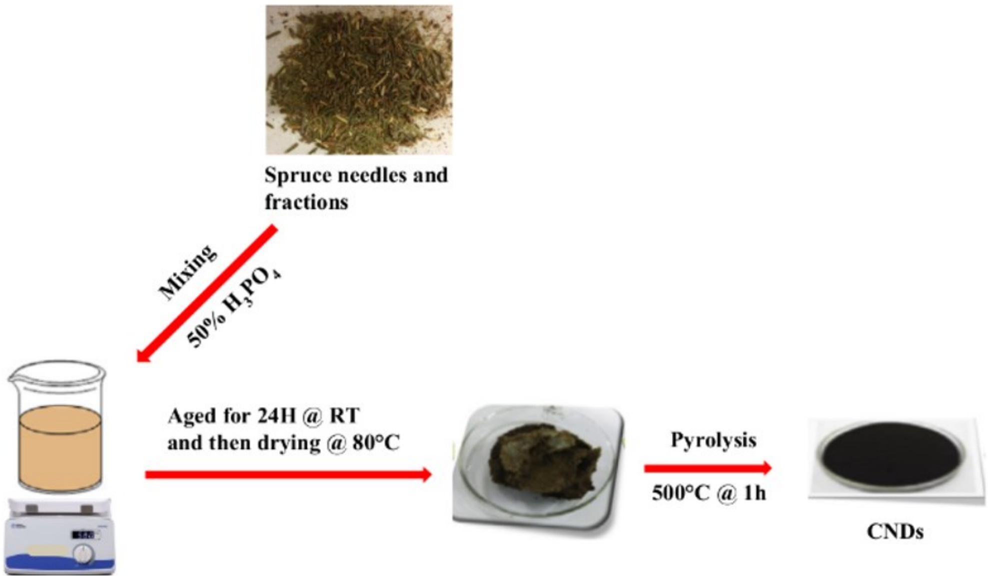


Figure 2.14: Synthesis path for the N-CNDs

2.5 Preparation of N-CND ink:

The fusion of materials and electrochemistry represents a focused foray into exploring solutions to key global sustainability challenges. In the context of this study, the fusion of nitrogen-rich carbon nano-dots and electrodes emerges not only as a harbinger of transformations in the field of electroreduction, but also as a potentially innovative source in the ongoing quest to address the most pressing challenges facing appear on the horizon.

Nitrogen plays a crucial role in N-CNDs utilized as electrodes for various reasons. Firstly, nitrogen doping introduces additional active sites on the carbon structure, enhancing the material's electrochemical activity. Additionally, nitrogen can modify the electronic properties of carbon nanodots, thereby improving electrical conductivity. The presence of nitrogen functionalities alters the surface chemistry of carbon nanodots, influencing their interactions with ions or molecules during electrochemical reactions and resulting in increased catalytic activity.

Furthermore, nitrogen doping contributes to the stability of the electrode material, rendering it more resistant to degradation during repeated electrochemical cycling. Acting as a dopant, nitrogen brings about improved charge carrier mobility, leading to enhanced overall electrochemical behaviour.

In the electrode preparation process, a meticulously synthesized catalyst, specifically 10 milligrams of N-doped Carbon Nano Dots (N-CND), was combined with a solution comprising 30 microliters of Nafion 117 and 970 microliters of ethanol. The resultant mixture underwent a thorough blending and sonicating procedure, extending over a duration of 30 minutes, until it transitioned into a uniformly homogeneous slurry.

Subsequently, a 50-microliter aliquot of this prepared slurry was coated onto a carbon paper possessing a geometric area measuring approximately 0.5 by 2.0 square centimetres (specifically, Toray Carbon Paper, TGP-H-090). This coated electrode was then left to air-dry at room temperature, allowing the solvents to evaporate and thereby facilitating the solidification of the electrode material. Tables 2.3 and 2.4 highlight all the quantities used both for the formation of the N-NCDs and the final electrode.

Table 2.3: Table for materials for the N-CND

Material for N-NCD	**Quantity**
Spruce Needels	10 g
Phosporic Acid 50%	20 g
Hot deionized water (90°C)	Not Quantified

Figure 2.4: Table for materials for the N-CND ink (Electrode)

Material for the N-CND ink	**Quantity**
N-CND	10 mg
Nafion 117	30 microliters
Ethanol	970 microliters
Carbon Paper	0.5x2 cm^2

2.6 Instrumentation

2.6.1 FT-IR

To comprehensively characterise the desorption process (DES) following carbon dioxide (CO_2) absorption, we employed attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). This technique took advantage of the advanced capabilities of the Bruker Vertex 80v FT-IR spectrometer, equipped with a highly sensitive DTGS detector.

ATR-FTIR spectroscopy, a powerful analytical tool, uses modulated energy in the infrared spectral region to examine the properties of a given sample. This method exploits the interaction of infrared radiation with the sample, which leads to the absorption of light at specific frequencies. These specific frequencies correspond directly to the vibrational energy levels of the chemical bonds existing between atoms within the molecular structure. In the study conducted, this analytical technique was used to investigate DES which by their nature are in liquid form and DES following the absorption of CO_2. In terms of the measurable concentration range using this technique, FTIR is frequently applied for concentrations ranging from 0.1% to 1%. Additionally, it exhibits sensitivity to trace concentrations, often in the realm of parts per million (ppm) or even parts per billion (ppb). With this analytical technique, in the current analysis, we employ it to investigate the absorption of CO_2 occurring within the utilized Deep Eutectic Solvents (DES).

The results of our ATR-FTIR analyses are elaborated in the following sections, providing a detailed examination of the spectra recorded during the absorption process. These spectra were analysed on an individual basis, and each relevant graph is presented separately in the Results and Discussion section. This approach allows a more complete understanding of the intricate chemical and physical changes that occur during CO_2 adsorption using DES as a solvent. The image number 5 shows the equipment used during characterization.

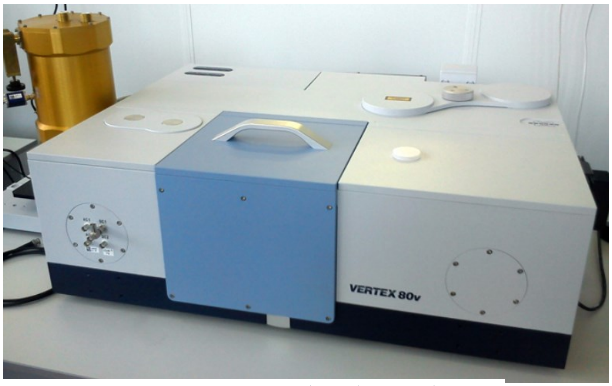


Figure 2.15: FTIR used in this study.

2.6.2 Viscometer

The Brookfield Viscometer was employed to assess the viscosity of deep eutectic solvents, both prior to and subsequent to CO_2 absorption. This type of viscometer measures the force required to keep a disc or cylinder rotating at a constant angular velocity immersed in the fluid to be measured. In this case, the force depends on the viscosity of the fluid. It is therefore necessary for the fluid to be brought to a working temperature.

The Brookfield Viscometer is a leading and exceptionally versatile instrument in the field of rheology and viscosity measurement. It plays a key role in elucidating the dynamic characteristics of various substances, including fluids, pastes and semi-solids, providing highly accurate viscosity assessments. What sets the Brookfield viscometer apart is its renowned accuracy in quantifying viscosity. Its ability extends over a wide range of viscosity ranges, making it a suitable choice in a wide variety of industries, ranging from food and pharmaceuticals to the intricacies of petrochemicals and cosmetics. In this analysis, approximately 0.75 mL of the substance is utilized, and the initial and crucial step involves the precise calibration of the measuring instrument. This calibration procedure is performed using the first sample prepared for the next measurement. It's important to note that calibration is a one-time procedure, remaining consistent for all subsequent sample measurements.

The table number 2.5 serves as an archive of the complete results derived from the battery of tests conducted at two distinct points in time: before and after carbon dioxide (CO_2) uptake. These results not only provide valuable insights into the evolution of substance properties, but also offer a quantitative and qualitative basis for examining the effects brought about by the CO_2 absorption process. All the measurements were carried out at 25 °C.

Table 2.5: Viscosity measurements for DESs

DES	***Viscosity [Cp] Before CO_2 absorption***	***Viscosity [Cp] After CO_2 absorption***	***% change during the absorption***
Im-MEA (1:2)	6.86	466.87	6709.08
Im-MEA (1:3)	10.15	510.45	4929.06
Im-MEA (1:4)	13.27	584.56	4305.12
Im-DEA (1:2)	0.13	40.74	31238
Im-PEHA (1:2)	55.40	122.58	121.26

The graph presented below (Figure 2.16) visually demonstrates the variations in viscosity, serving as empirical support to discern the alterations before and after the absorption of CO_2.

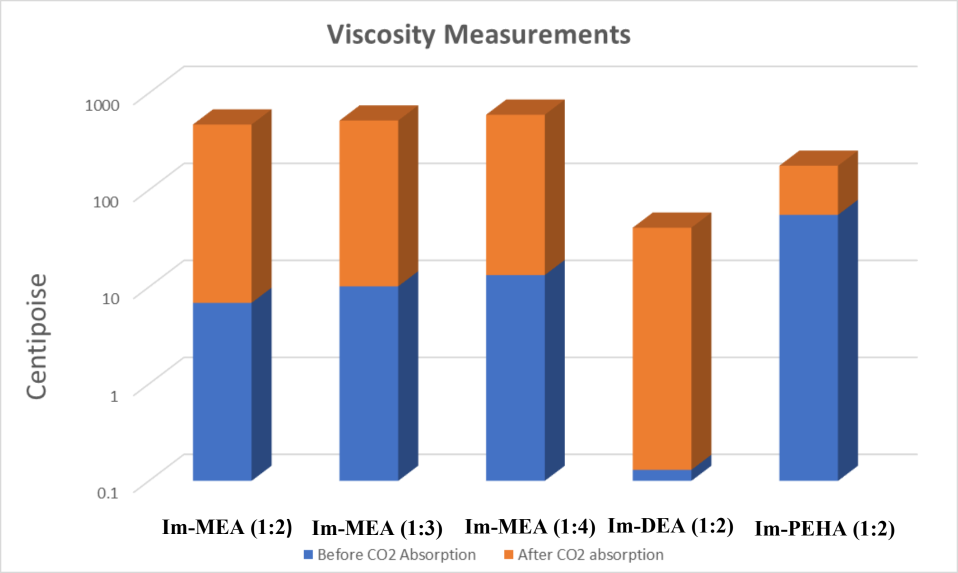


Figure 2.16: Change in viscosity before and after CO2 absorption.

Viscosity studies play a pivotal role in understanding the behaviour of various substances, and they become particularly significant in the context of Deep Eutectic Solvents (DES).

Within the realm of DES, it is essential to differentiate between two distinctive phases of absorption: chemical and physical. The chemical absorption is the predominant mechanism, driving notable changes in the solvent's properties and, in particular, its viscosity. The chemical absorption process, characterized by its relatively longer duration, allows for a comprehensive investigation of viscosity alterations. This is because the chemical reactions involved often result in the formation of new molecular species, intermolecular interactions, and altered molecular configurations, all of which significantly impact the solvent's viscosity.

In contrast, the physical absorption phase within DES is often ephemeral, lasting for a relatively short period. This transience hinders the thorough examination of viscosity changes, as it does not provide sufficient time to observe and understand structural changes or interactions that would lead to significant viscosity changes.

Therefore, the focus of viscosity investigations in DES naturally gravitates toward the chemical absorption process due to its extended duration and pronounced impact on the physical properties of the solvent.

2.6.3 NMR

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that has revolutionized the study of molecular structures, providing valuable information on the composition, connectivity and environment of atoms within a molecule. Two important branches of NMR spectroscopy are proton NMR (H-NMR) and carbon NMR (C-NMR), each with their own unique capabilities and applications.

Proton NMR, often referred to as H-NMR, focuses on the nuclei of hydrogen atoms within a molecule.

In contrast to H-NMR, Carbon NMR (C-NMR) spectroscopy focuses on the nuclei of carbon atoms. While it may not offer the same level of detailed structural information as H-NMR, C-NMR plays a pivotal role in the characterization of carbon-containing compounds. C-NMR provides data on the different types of carbon atoms in a molecule and quantifies the carbon content in various compounds. Both proton nuclear magnetic resonance (H-NMR) spectroscopy and carbon-13 nuclear magnetic resonance (C-NMR) spectroscopy play crucial roles in various scientific disciplines, such as chemistry, biochemistry, and materials science. In the study conducted, these analytical techniques were primarily employed to examine DESs formed both before and after CO_2 adsorption. Furthermore, after electroreduction, the same techniques were used to study the liquids resulting from this transformation. This analytical technique proves highly valuable due to its extensive measurable concentration range. Capable of accommodating high concentrations ranging from tens of millimoles to a few moles per liter, it is frequently applied for concentrations in the millimolar range (mM). This range is standard for studying a wide array of organic and inorganic compounds in solution.

Figure 2.17: NMR used in the study.

2.6.4 GC-MS

Gas chromatography (GC) combined with a mass spectrometer (MS) detector represents a dynamic and versatile analytical instrument that has revolutionized the field of chemical analysis. This powerful combination of techniques offers unprecedented capabilities in separating, identifying, and quantifying complex mixtures of chemical compounds.

Gas chromatography is a well-established chromatographic method that allows the separation of volatile compounds based on their chemical properties, such as boiling points and affinities for the stationary phase. In contrast, mass spectrometry is a highly sensitive and specific technique for determining the molecular composition of compounds by measuring their mass-to-charge ratios and analyzing their fragment patterns.

When these two analytical powerhouses are brought together in a single instrument, it creates a GC-MS system that can provide a wealth of information about the constituents of a sample. This technology is widely utilized in fields ranging from environmental analysis, pharmaceuticals, and food safety to forensics and clinical diagnostics, making it an indispensable tool for researchers and analysts alike.

The analytical technique in question plays a key role in the later stages of the study reported here, particularly in the conversion phase. Its main function is the meticulous examination and interpretation of the gases generated and accumulated within the electroreduction cell. These gases are by-products of the intricate and ecologically significant conversion of carbon dioxide (CO_2) through the medium of deep eutectic solvents (DES).

The method of analysis, with its precision and comprehensiveness, serves as an indispensable tool in this context. By scrutinizing the composition, concentration, and specific identities of the gases formed during electroreduction, it provides invaluable insights.

2.6.5 BET

The BET (Brunauer-Emmett-Teller) characterization technique is a widely used method for determining the surface area of porous materials, such as catalysts, adsorbents, and nanoparticles. It was developed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in the early 20th century. Key aspects of the BET characterization technique include:

- *Adsorption Isotherms*: BET analysis relies on the measurement of adsorption isotherms. In this process, a gas (typically nitrogen) is introduced to a solid material at different pressures and temperatures. The gas molecules adsorb onto the material's surface, and the quantity of gas adsorbed is recorded.
- *Monolayer Adsorption:* The BET method is based on the assumption that the first layer of adsorbed gas molecules forms a complete monolayer on the material's surface. This means that gas molecules occupy all available surface sites in a single layer before multilayer adsorption occurs.
- *BET Equation*: The BET equation is the mathematical foundation of this characterization technique. It relates the amount of gas adsorbed (P/P_0) at a given relative pressure (P/P_0) to the surface coverage.

In the context of the study at hand, the BET characterization technique played a pivotal role in the comprehensive assessment of various Carbon Nanodots (CNDs) that were synthesized. The objective was to discern which among these CND variants exhibited the highest potential and suitability for the specific purpose being pursued.

2.6.6 *TPD*

Temperature Programmed Desorption (TPD) is a versatile and powerful characterization technique widely used in the fields of surface science, catalysis, materials science, and environmental science. Temperature Programmed Desorption (TPD) is primarily focused on elucidating the dynamic desorption behaviour of molecules or atoms from the surface of a solid material. This technique involves subjecting the material to a precisely controlled temperature ramp, all while closely monitoring the evolution of desorbed species as a function of temperature. TPD's significance is especially pronounced in its ability to delve into the interaction dynamics between adsorbates—such as gases or molecules—and the surface of the material.

A central facet of TPD is its capacity to unveil the intricacies of adsorption sites inherent to the material's surface and discern the energies at which adsorbates are bound. This critical information is crucial in decoding the reactivity and selectivity of the material.

TPD's capacity to unravel the surface chemistry and desorption kinetics within solid materials positions it as a cornerstone in the realms of materials science, catalysis, and surface engineering.

In the present research work, the use of this characterisation method takes centre stage as we navigate the landscape of carbon nanodots (CNDs). The overall objective is to evaluate a number of synthesised CNDs and discern, with a discerning eye, which of these variants stands out as the most promising and skilful in the context of our specific research objective.

2.6.7 *EDX*

Energy-Dispersive X-ray Spectroscopy (EDX) is a fundamental and highly effective characterization technique used in a multitude of scientific fields, from materials science to geology and biology.

This technique is essential for investigating the elemental composition of a wide range of materials, providing invaluable insights into their chemical makeup, distribution, and spatial organization.

In our research, we employed this technique to conduct a meticulous and in-depth analysis of the selected N-rich Carbon Nanodot (N-CND).

2.7 THERMODYNAMIC MODEL

2.7.1 CO_2 Absorption

The absorption of carbon dioxide (CO_2) in certain solvents occurs through two distinct mechanisms, each with its own characteristics:

1. *Chemical Absorption:* Within the realm of carbon dioxide (CO_2) capture and absorption processes, chemical absorption represents a fundamental mechanism of interaction between a solvent or absorbing medium and the CO_2 absorbate. This mechanism is defined by the formation of chemical bonds between the absorbing molecule and the CO_2 molecules. These bonds are predominantly covalent in nature, reflecting the sharing of electron pairs between the solvent molecules and the CO_2 species. One of the distinctive features of chemical absorption is its capacity to lead to the formation of entirely new chemical compounds. In the context of CO_2 capture, this translates into the conversion of gaseous CO_2 into distinct chemical entities, often involving the incorporation of carbon atoms from CO_2 into the molecular structure of the solvent. These chemical transformations represent a pivotal step in the absorption process.
   Furthermore, chemical absorption is fundamentally an irreversible process. Once the CO_2 molecules have undergone chemical reaction with the solvent, they become an integral part of the newly formed compounds, and reversing this transformation typically requires a different set of chemical reactions or energy-intensive processes. In essence, the CO_2 molecules are no longer easily extractable from the solvent, making chemical absorption a crucial aspect of strategies aimed at permanently sequestering or transforming CO_2 into less harmful forms. By facilitating the permanent bonding and transformation of CO_2, chemical absorption plays a pivotal role in addressing environmental concerns related to greenhouse gas emissions and contributes to the development of sustainable solutions for a more carbon-neutral future.

2. *Physical Absorption:* In the domain of carbon dioxide (CO_2) capture, physical absorption represents a distinct mode of interaction between a solvent or absorbent medium and gaseous CO_2. Unlike chemical absorption, which involves the formation of chemical bonds and irreversible transformations, physical absorption hinges entirely on the influence of physical forces. The physical forces at play in this process encompass a range of intermolecular interactions, including but not limited to Van der Waals forces, dipole-dipole interactions, hydrogen bonding, and other intermolecular attractions. These forces arise due to the electric charge distribution within molecules and, crucially, do not culminate in the creation of novel chemical compounds. Instead, they manifest as temporary, non-covalent attractions that occur between the solvent molecules and CO_2. Crucially, what distinguishes physical absorption is its reversibility. In other words, CO_2 molecules that have been physically absorbed into the solvent can be readily released under appropriate conditions. This means that altering temperature,

pressure, or other environmental factors can cause the CO_2 molecules to detach from the solvent, thus allowing for their recovery or re-release into the atmosphere. Physical absorption has garnered attention for its capacity to provide a flexible and adaptable means of CO_2 capture, where the absorbed gas can be subsequently desorbed and collected, making it a more dynamic process compared to the permanent transformation of chemical absorption. This characteristic has important implications for carbon capture and storage strategies, offering options for controlled CO_2 release and reuse, contributing to the development of sustainable and economically viable solutions for addressing climate change and reducing CO_2 emissions.

2.7.2 Equation model for the absorption

In order to comprehensively characterize the overall absorption of CO2 within solvent systems, which encompasses both chemical and physical absorption phenomena, a powerful tool known as the Reaction Equilibrium Thermodynamic Model (RETM) has been employed [17].
This model has gained recognition for its remarkable accuracy in correlating CO_2 solubility in pure Task-Specific Ionic Liquids (TSILs). It achieves this by utilizing two fundamental principles:

- *Henry's Law*: Henry's law is a fundamental concept used to elucidate the correlation between the concentration of a gas, in our case CO_2, within a liquid and the partial pressure of that gas in the adjacent gaseous phase. This principle serves as a cornerstone for comprehending the intricate dynamics by which temperature and pressure exert their influence on the solute's CO_2 concentration within the solvent.

- *Reaction Equilibrium*: This aspect of the Reactive Equilibrium Thermodynamic Model (RETM) encompasses an essential consideration: the dynamic nature of the chemical reactions that can occur during carbon dioxide (CO_2) uptake. This is the critical concept of establishing the chemical equilibrium between the absorbed CO_2 and the solvent within the system. In this way, the model provides a complex and general perspective of the solubility of CO2 in task-specific ionic liquids (TSILs). By taking these chemical reactions into account, the RETM not only quantifies the solubility of CO_2 in TSILs, but also reveals a deeper understanding of the complex interaction between CO_2 and the solvent, thereby improving our ability to predict and optimise CO_2 capture and separation processes.

By seamlessly integrating Henry's law and reaction equilibrium, the RETM presents an exceptionally comprehensive and accurate framework for studying the intricate mechanisms involved in the uptake of carbon dioxide (CO_2) within deep eutectic solvents (DESs).
This sophisticated model serves as a valuable tool, providing a deep understanding of the solubility of CO_2 in DES compounds and facilitating the formulation of strategic approaches for carbon capture and mitigation of greenhouse gas emissions.

The absorption of carbon dioxide (CO_2) can occur through two distinct mechanisms within Deep Eutectic Solvents (DES). These processes are as follows:

- *Single Molecule Reaction:* In this mode of CO_2 absorption, a DES molecule forms a chemical bond with a single CO_2 molecule. This reaction involves the bonding of a DES molecule with one of the oxygen atoms in the CO_2 molecule, resulting in the formation of charged species. The reaction can be described as follows:

  $$RNH_2 + CO_2 \rightarrow RNHH^{+}COO^{-} \tag{2.1}$$

  Here, RNH2 represents DES where R is the inherent part of imidazole, and CO_2 undergoes a chemical transformation, creating charged specie, $RNHH^{+}COO^{-}$.

- *Double Molecule Reaction:* In this mechanism, two DES molecules engage with two CO_2 molecules, and together, they establish two separate bonds, one with each of the oxygen atoms in the CO_2 molecule. This leads to the formation of charged species, reflecting the cooperative nature of this reaction. The chemical equation for this process is as follows:

  $$2RNH_2 + 2CO_2 \rightarrow RNHCOO^{-} + RNH_3^{+} \tag{2.2}$$

The equations representing both physical and chemical absorption processes are detailed as follows, elucidating the distinct mechanisms at play in each of these fundamental phenomena.
Physical absorption refers to the mechanism by which a gas, such as carbon dioxide (CO_2), is dissolved into a liquid or solvent through intermolecular forces, without undergoing any chemical reactions.
The equilibrium that characterizes the physical absorption is typically governed by Henry's law, which states that the solubility of the gas in the liquid is directly proportional to the partial pressure of the gas in the surrounding atmosphere.
The Henry's law equation can be succinctly expressed as:

$$P = H\gamma_{CO_2}m_{CO_2} \tag{2.3}$$

In this context, " P " denotes the pressure of the CO_2 in bar, " H" represents the Henry's law constant expressed in units of bars, "m_{CO_2}" signifies the molality of the unbound CO_2 dissolved within the DES, and "γ_{CO_2}" stands for the coefficient of the corresponding species in the liquid phase.

The equilibrium in chemical absorption is influenced by the specific reaction kinetics, including reaction rates and thermodynamics.

The equilibrium equations for the chemical reactions involving Deep Eutectic Solvents (DES) and carbon dioxide (CO_2) can be elaborated as follows:

1) *Reaction Equilibrium Equation for the Reaction with One Mole of DES and One Mole of CO_2 (K_1):*

For this reaction, one mole of DES interacts with one mole of CO_2, resulting in the formation of specific chemical species, including $RNHH^+COO^-$.

The equilibrium constant K_1 is expressed as:

$$K_1 = \frac{\gamma_{RNHH^+COO^-}\frac{m_{RNHH^+COO^-}}{m_0}}{\frac{P}{P_0}\gamma_{RNH_2}\frac{m_{RNH_2}}{m_0}} \tag{2.4}$$

In this equation:

- $\gamma_{RNHH^+COO^-}$ represents the activity coefficient of the $RNHH^+COO^-$ species.
- $m_{RNHH^+COO^-}$ is the molar concentration of $RNHH^+COO^-$ in the solution.
- m_0 signifies the initial molar concentration of the species involved.
- P is the partial pressure of CO_2 in the gas phase.
- P_0 is the reference partial pressure.
- γ_{RNH_2} denotes the activity coefficient of the RNH_2 species.
- m_{RNH_2} is the molar concentration of RNH_2 in the solution.

2) *Reaction Equilibrium Equation for the Reaction with Two Moles of DES and One Mole of CO_2 (K_2):*

In this scenario, two moles of DES molecules react with one mole of CO_2, leading to the formation of $RNHCOO^-$ and RNH_3.

The equilibrium constant K_2 is expressed as:

$$K_2 = \frac{\gamma_{RNHCOO^-RNH_3^+}\frac{m_{RNHCOO^-RNH_3^+}}{m_0}}{\frac{P}{P_0}\gamma_{RNH_2}\frac{m_{RNH_2}}{m_0}} \tag{2.5}$$

In this equation:

- m_0 signifies the initial molar concentration of the species involved.
- P is the partial pressure of CO_2 in the gas phase.

- P_0 is the reference partial pressure.
- $\gamma_{RNHCOO^{-}RNH_3^{+}}$ is the coefficient of $RNHCOO^{-}RNH3^{+}$ species in the liquid phase.
- γ_{RNH_2} denotes the activity coefficient of the RNH_2 species.
- m_{RNH_2} is the molar concentration of RNH_2 in the solution.
- $m_{RNHCOO^{-}RNH_3^{+}}$ is the molality of the free CO_2 dissolved in the complex (RNHCOO-RNH3+).

The determination of the activity coefficients for CO_2, RNH_2, RNHCOO and $RNHCOORNH_3$ within the reaction system is a major challenge. In light of this complexity, the choice was made to adopt a simplified approach to avoid the intricate task of calculating these coefficients.

Rather than delve into the complexity of these calculations, an assumption was made that could be considered bold but convenient. This is to consider the activity coefficients of CO_2, RNH_2, RNHCOO and $RNHCOORNH_3$ as having a constant unit value throughout the entire absorption process.

By making this assumption, we effectively simplify the non-ideal behaviour of the system by encapsulating it in the representation of only three key parameters: H, K_1 and K_2. This practical and heuristic approach simplifies the modelling and analysis of the reaction system, allowing us to focus on the broader dynamics and trends of the process. In this way, we can gain valuable insights and predictions without being constrained by the intricate nature of the activity coefficients.

In the context of the chemical reaction involving the complex interaction between a DES molecule and a CO_2 molecule, precisely designated as reaction number (2.1), we have the ability to extrapolate and elucidate the underlying equation that governs this fascinating process. The ensuing equation is provided below, functioning as the focal element that unveils the intricate molecular dynamics in action during this chemical event.

$$m_{CO_2}^{t} = \frac{P}{H} + \frac{m_{DES}^{t} K_1}{1+K_1\left(\frac{P}{H}\right)}\left(\frac{P}{H}\right) \tag{2.6}$$

Regarding the equation linked to reaction number (2.2), wherein two distinct molecules of Deep Eutectic Solvent (DES) undergo a chemical transformation in the presence of a single carbon dioxide (CO_2) molecule, let's delve deeper into the specifics. The equation that characterizes this reaction is as follows:

$$m_{CO_2}^{t} = \frac{P}{H} + \frac{2m_{DES}^{t} K_2}{1+K_2\left(\frac{P}{H}\right)^2}\left(\frac{P}{H}\right)^2 \tag{2.7}$$

In this equation, the numerical subscript "2" is indicative of the formation of a chemical bond involving the two DES molecules, which is a crucial feature of this reaction. It highlights the intricate interaction that occurs between the two DES molecules and a solitary CO_2 molecule during the course of this chemical process.

The equation, by its very nature, serves as a foundational representation of this intriguing chemical phenomenon, shedding light on the intricacies of the bonding and transformations involved in the reaction.

The subsequent equation, which I'll refer to as the Reactive Equilibrium Thermodynamic Model (RETM) equation, has been formulated as a means to establish a comprehensive correlation between the overall solubility of carbon dioxide (CO_2) in Deep Eutectic Solvents (DESs) and the partial pressure of CO_2.

This equation is derived through a straightforward deductive process, combining, and synthesizing the aforementioned equations.

$$m_{CO_{2,0}} = \frac{P}{H} + \frac{m_{RNH_{2,0}}}{2} + \frac{(1-K_1^2P^2)\left[1-\sqrt{\frac{8m_{RNH_{2,0}}K_2P}{(1+K_1P)^2}+1}\right]}{8K_2P} \tag{2.8}$$

The RETM equation encapsulates a complex relationship that encapsulates the fundamental interplay between CO_2 solubility and the partial pressure of CO_2, drawing from the principles elucidated in the previous equations. It represents a pivotal step in understanding the dynamic equilibrium of CO_2 dissolution within DESs.

Next, this equation is solved with the help of a specialised software tool, namely MatLab, which facilitates the calibration and fitting process. The solution is found by fitting with known solubility data from previously performed solubility tests. Using this software, known variables such as the partial pressure (P) and the concentration of the reactive solvent components (m_{RNH2O}) are added to the unknown variables, namely the Henry's Law constants for physical absorption (H) and the equilibrium constants for chemical absorption (K_1 and K_2).

By harnessing the computational power and optimization algorithms offered by MatLab, this comprehensive system of equations is analysed, and a solution is derived. This equation allows us to correlate experimental measurements and predict solubility under non-experimentally investigated conditions. The outcome of this process is the precise amounts of carbon dioxide that are chemically absorbed and physically absorbed within the given system. This computational approach not only streamlines the determination of these critical parameters but also enhances our understanding of the interplay between chemical and physical mechanisms in the CO_2 absorption process, thus advancing our capabilities in carbon capture and storage research and technology.

In the subsequent chapter, the comprehensive analysis and interpretation of the graph illustrating the results of the equation will be undertaken in meticulous detail. The following section will delve into a thorough examination of the graphical representation, aiming to unveil its intricacies and the underlying trends. Through a methodical exploration of the visual data, the aim is to extract valuable insights and draw connections that contribute to a nuanced comprehension of the subject matter.

2.8 REACTION MECHANIMS

2.8.1 CO_2 Absorption into DES

In this section, we present a comprehensive overview of how a DES molecule interfaces with carbon dioxide.

The reaction mechanism between a molecule of deep eutectic solvent (DES), specifically imidazole-monoethanolamine (Im-MEA) in the molar ratio of 1:2, and carbon dioxide (CO_2) typically involves a series of steps. The adsorption mechanism predominantly involves the formation of a zwitterion, a process visually represented in the accompanying figure. Im-MEA is a common component in DES formulations. Here's a simplified explanation of the reaction mechanism:

- *Step 1: CO_2 Absorption:*

When CO_2 is introduced to the DES solution, it begins to dissolve in the solvent. The absorption process is primarily driven by the interaction between CO_2 and the functional groups within Im-MEA.

- *Step 2: Formation of Carbamate:*

In the presence of CO_2, Im-MEA can undergo a chemical reaction to form a carbamate. The carbamate is typically formed through the following reaction:

$$CO_2 + \text{Im-MEA (Protonated)} \text{ -> } \text{Carbamate Ion} \qquad (2.9)$$

The protonated Im-MEA acts as a nucleophile and attacks the electrophilic carbon in CO_2, forming a carbamate ion.

- *Step 3: Proton Transfer:*

Proton transfer reactions may occur within the DES, as Im-MEA can act as a Brønsted-Lowry base and CO_2 as a Brønsted-Lowry acid. These proton transfer reactions help in stabilizing the carbamate ion and maintaining the overall charge balance within the solution.

- *Step 4: Ionic Association:*

The carbamate ion may interact with other ions present in the deep eutectic solvent. DESs are often composed of multiple components, and the interaction of these components with the carbamate ion may further enhance CO_2 absorption.

- *Step 5: Solvent Regeneration:*

After the absorption of CO_2, the loaded DES is typically regenerated to release the captured CO_2. Regeneration is usually achieved by changing the conditions, such as increasing temperature or reducing pressure, which helps to desorb the CO_2 from the solvent.

It's important to note that the specific reaction mechanism can vary depending on the composition of the deep eutectic solvent and the experimental conditions. Different DES formulations may exhibit variations in their reaction pathways and kinetics.

In this elucidation, we have focused on one of the two deep eutectic solvents (DES) that have demonstrated remarkable efficiency in the context of carbon dioxide (CO_2) absorption. It is important to note that the mechanism described here can be considered a generalized representation, as the interaction between deep eutectic solvents and CO_2 typically follows a consistent pattern across different DES formulations.

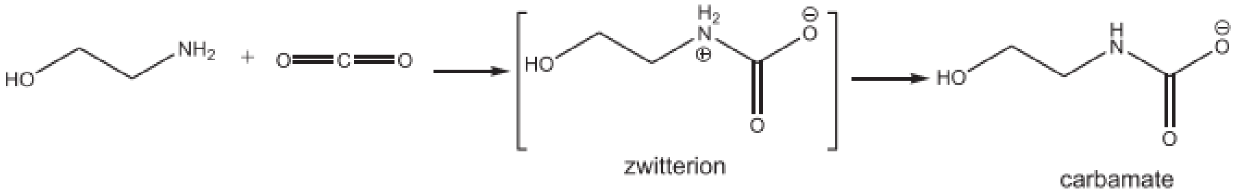


Figure 2.18: Reaction Mechanism for the Carbamate formation

2.8.2 Electroreduction of CO_2 into CO

The electroreduction of carbon dioxide (CO_2) employing deep eutectic solvents (DES) unfolds through a series of well-defined steps, with each stage underpinned by precise chemical reactions. This intricate process can be elucidated as follows:

- *Step 1: Adsorption of CO_2*

CO_2 molecules are adsorbed on the surface of the working electrode (usually a metal electrode) as follows:

$$CO_2 (g) \rightleftharpoons CO_2 (ads) \quad (2.10)$$

- *Step 2: Formation of CO_2 Radical Anion*

CO_2 adsorbed on the electrode is reduced to form a CO_2 radical anion (CO_2•-) by gaining an electron:

$$CO_2 (ads) + e^- \rightleftharpoons CO_2{\bullet}- \quad (2.11)$$

- *Step 3: Protonation of CO_2•-*

The CO_2 radical anion reacts with a proton from the DES to form bicarbonate (HCO_3^-):

$$CO_2^{\bullet -} + H^+ \rightleftharpoons HCO_3^- \tag{2.12}$$

- *Step 4: Electrochemical Reduction to CO*

The HCO_3^- species is further reduced to form carbon monoxide (CO):

$$HCO_3^- + e^- \rightleftharpoons CO + OH^- \tag{2.13}$$

- *Step 5: Desorption of CO*

The formed CO may desorb from the electrode surface:

$$CO\ (ads) \rightleftharpoons CO\ (g) \tag{2.14}$$

In the above reactions, the deep eutectic solvent acts as an electrolyte, facilitating the movement of ions and charge carriers (electrons) between the working and counter electrodes, allowing for the reduction of CO_2 to CO. What makes it intriguing is that, owing to its unique properties, the ion transfer rate surpasses that of other electrolytes. For instance, aqueous electrolytes, such as traditional acidic or alkaline solutions.

It is crucial to note that the specific reactions and intermediates involved can vary contingent upon factors such as the composition of the electrode, the unique properties of the DES, and the electrochemical conditions applied. Additionally, the introduction of catalysts and distinct reaction parameters can exert a profound influence on the reaction pathways and product selectivity.

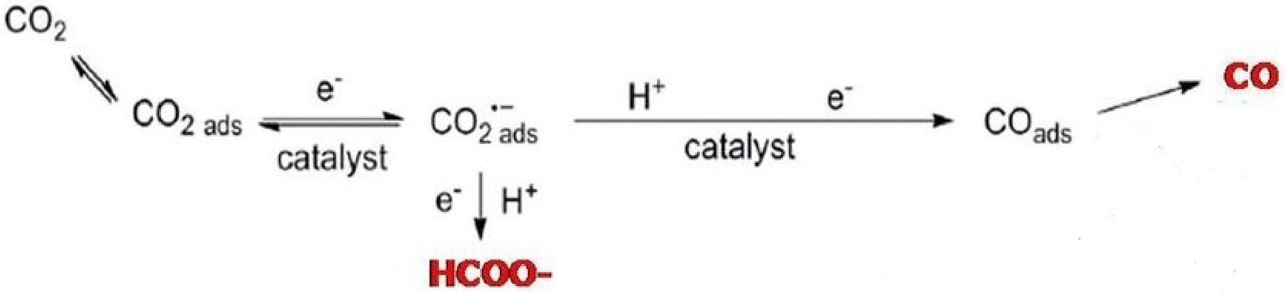


Figure 2.19: Path for the Electroreduction of CO_2 into CO [18]

2.9 Critical properties

2.9.1 *Group functional method*

The development of innovative processes involving deep eutectic solvents (DES) requires a comprehensive understanding of their physical, physico-chemical and transport properties. A thorough understanding of the thermodynamic behaviour of mixtures containing DES becomes indispensable to unlock the full potential of these solvents.

Phase equilibrium data clarify how DESs interact with other components in a mixture, shedding light on their ability to dissolve, separate or react with different compounds. Furthermore, the thermodynamic characteristics of mixtures incorporating DES are key to improving the efficiency and environmental friendliness of a wide range of applications.

The formulation of robust thermodynamic models requires the availability of reliable experimental data on phase equilibrium and essential thermophysical information. Unfortunately, there is a considerable paucity of studies dedicated to the determination of these properties. The main factor contributing to the slow pace of this research lies in the challenge posed by the fact that a significant portion of synthesised DES exhibit a predisposition to decomposition when approaching temperatures close to their typical boiling points. Consequently, the scarcity of such data poses a constraint on the development of predictive models, effectively limiting our complete understanding of DES characteristics.

The critical properties of deep eutectic solvents play a key role in characterising their behaviour under different conditions, influencing their applications, stability, and overall effectiveness in various processes.

In the focal study of this thesis, the search for critical properties, in particular the acentric factor, serves to characterise the deep eutectic solvents (DES) formed and to assess which deviates more from non-sphericity of molecular structures within a given fluid.

In a recent development, Rebelo and their research colleagues [19] have introduced a novel method designed to estimate the critical temperature of specific ionic liquids. This innovative approach hinges on the utilization of the temperature-dependent variations in surface tensions and liquid density of these ionic liquids. The research conducted by Rebelo, and their team stands out as a noteworthy addition to the ongoing efforts aimed at unravelling the thermophysical properties of ionic liquids. The critical temperature of an ionic liquid holds paramount importance in numerous applications, particularly in the context of phase transitions, solvation phenomena, and as a fundamental parameter in the design and optimization of processes involving these compounds. The authors of the study employed empirical equations put forth by Eotvos and Guggenheim.

They substantiated their proposal through the estimation of critical and normal boiling temperatures for 90 compounds with known Tc and/or Tb values. This dataset enabled them to determine the normal boiling temperature and critical properties of various ionic liquids. Their work, as conducted by Rebelo et al., exhibited a commendable level of accuracy, surpassing a 10% margin of error.

In the pursuit of crafting thermodynamic models that are well-suited for the characterization of both individual pure components and complex mixtures, the acquisition of a deep and comprehensive understanding of critical properties and various other fundamental physical parameters is an irreplaceable cornerstone. Critical properties, encompassing parameters like critical temperature (T_c), critical pressure (P_c), and critical molar volume (V_c), serve as pivotal reference points that govern phase behaviour and equilibria in a wide range of chemical systems.

Among the multifarious methodologies available for the calculation and estimation of these thermodynamic properties, the group contribution method stands out as a principal and extensively embraced paradigm. This approach leverages the collective impact of chemical functional groups within molecules to predict the thermophysical properties of substances. Over time, the group contribution method has emerged as a cornerstone in the domain of thermodynamics, having been applied in a myriad of research and industrial settings to estimate critical properties and other relevant parameters for a diverse spectrum of chemical compounds. Its enduring appeal lies in its capacity to offer reasonable estimates for a wide array of substances, even when comprehensive experimental data is scarce or unavailable.

An exemplary illustration of this concept can be found in the work of Joback and Reid [20], whose methodology enjoys widespread recognition in academic literature and finds versatile applications across various domains.

The distinctive feature of this method lies in its approach to property estimation, in which the determination of a specific property for a compound involves summing the contributions of all atom groups present in the molecule. At the same time, this method takes into account the frequency of occurrence of each group, which is essentially a count of how many times a particular group of atoms is iterated within the molecular structure. This approach offers a significant advantage in that it can produce highly accurate estimates of properties while maintaining efficiency and avoiding the need for computationally intensive calculations.

By assigning relative weights to different groups of atoms based on their frequency and their impact on the property of interest, this method simplifies the property estimation process. As a result, it offers a rapid and straightforward means of approximating these properties, even for compounds with intricate molecular structures. This efficiency is particularly advantageous, as it enables researchers and practitioners to make quick, yet reliably accurate predictions without the need for complex and resource-intensive computational simulations.

Lydersenn [21] made a pioneering contribution to this field by introducing a comprehensive framework comprising 43 distinct structural groups and their equations for calculating various properties. This marked a significant milestone in the early stages of research in this field.

Joback and Reid [20], on the other hand, further extended this foundation by outlining 42 structural groups and developing a wide range of equations suitable for evaluating these properties. Their substantial and meticulous work constituted a noteworthy advance, consolidating the evolution of methodologies in this area.

The model employed in this study is derived from Alvarez and Valderrama [22], who skillfully amalgamated the most favorable aspects of the Lydersen model with the strengths of the method introduced by Joback and Reid. This synthesis led to the development of the "Modified Lydersen-Joback-Reid" method, which has demonstrated a remarkable ability to yield accurate predictions, particularly for high-molecular-weight molecules.

This method intricately combines the predictive equations formulated by Lydersen, which pertain to critical pressure and critical volume, with the equations devised by Joback and Reid, which are specifically tailored for estimating the normal boiling temperature and the critical temperature of chemical compounds. This fusion of the Lydersen and Joback-Reid equations exploits the advantages of each, resulting in a more robust methodology for the characterisation of different molecular structures, which lends itself to a wide range of applications in the field of chemical thermodynamics and process design.

The essence of the Modified Lydersen-Joback-Reid method is encapsulated by a compact set of four fundamental equations, serving as the method's core framework. These are depicted below:

$$T_b = 198.2 + \sum n\Delta T_{bM} \tag{2.15}$$

$$T_c = \frac{T_b}{A_M + B_M \sum n\Delta T_M - (\sum n\Delta T_M)^2} \tag{2.16}$$

$$P_c = \frac{M}{[C_M + \sum n\Delta P_M]^2} \tag{2.17}$$

$$V_c = E_M + \sum n\Delta V_M \tag{2.18}$$

The parameters in the previous equation were calculated by the author and the results are shown here:

- A_M is set to a value of 0.5703.
- B_M is defined as 1.0121.
- C_M is determined as 0.2573.
- E_M is calculated as 6.75.

It should be noted that the parameter M corresponds to the average molecular weight of the substance in question, a key variable in this context.

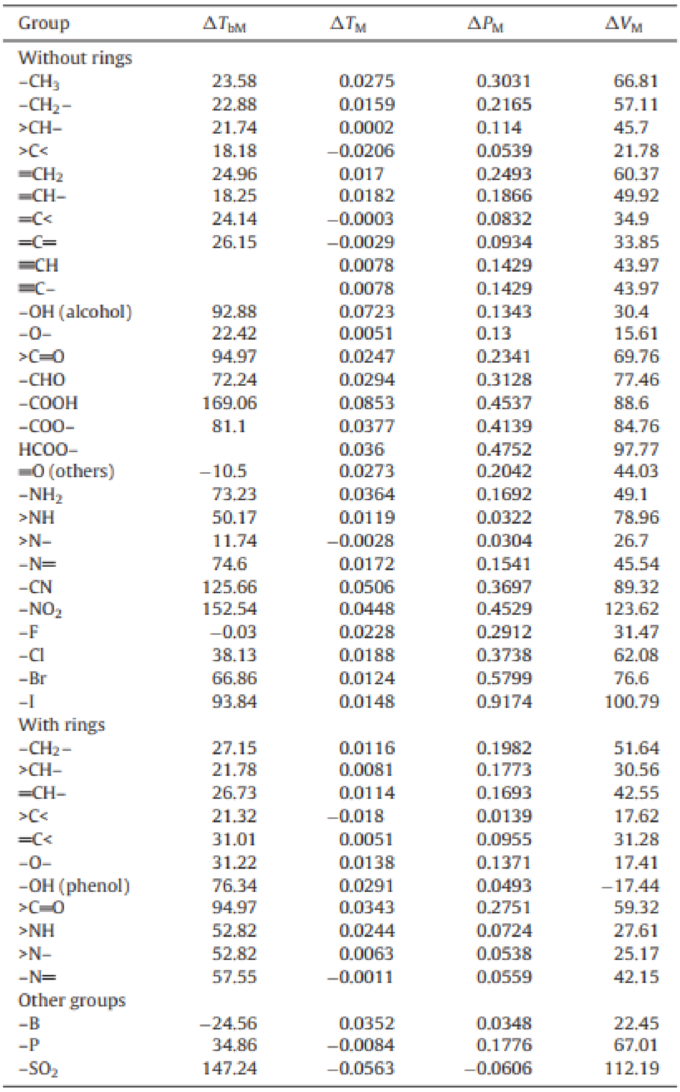
The equations highlighted in the previous lines refer to crucial properties, including the normal boiling temperature, the critical temperature, pressure, and volume of the substance under consideration.

2.9.2 *Extension of the method to ionic liquid/deep eutectic solvents*

Among the methods discussed earlier, the modified Lydersen-Joback-Reid approach has been employed to broaden its utility in forecasting the critical properties of ionic liquids. This expansion of the method was carried out in a straightforward manner by introducing three new functional groups: -B, $-SO_2$, and -P.

Valderrama and Robles conducted an analysis of the effects on T_b, T_c, P_c, and V_c using an approach closely aligned with the one elucidated by Alvarez and Valderrama [23]. The specific values for these groups are succinctly presented in the accompanying table. This table also provides a comprehensive overview of all group values pertinent to this method.

After ascertaining the values for the three novel groups (-B, $-SO_2$, -P), the critical properties, acentric factors, and normal boiling temperatures were subsequently determined.



Group	ΔT_{bM}	ΔT_M	ΔP_M	ΔV_M
Without rings				
$-CH_3$	23.58	0.0275	0.3031	66.81
$-CH_2-$	22.88	0.0159	0.2165	57.11
>CH−	21.74	0.0002	0.114	45.7
>C<	18.18	−0.0206	0.0539	21.78
$=CH_2$	24.96	0.017	0.2493	60.37
=CH−	18.25	0.0182	0.1866	49.92
=C<	24.14	−0.0003	0.0832	34.9
=C=	26.15	−0.0029	0.0934	33.85
≡CH		0.0078	0.1429	43.97
≡C−		0.0078	0.1429	43.97
−OH (alcohol)	92.88	0.0723	0.1343	30.4
−O−	22.42	0.0051	0.13	15.61
>C=O	94.97	0.0247	0.2341	69.76
−CHO	72.24	0.0294	0.3128	77.46
−COOH	169.06	0.0853	0.4537	88.6
−COO−	81.1	0.0377	0.4139	84.76
HCOO−		0.036	0.4752	97.77
=O (others)	−10.5	0.0273	0.2042	44.03
$-NH_2$	73.23	0.0364	0.1692	49.1
>NH	50.17	0.0119	0.0322	78.96
>N−	11.74	−0.0028	0.0304	26.7
−N=	74.6	0.0172	0.1541	45.54
−CN	125.66	0.0506	0.3697	89.32
$-NO_2$	152.54	0.0448	0.4529	123.62
−F	−0.03	0.0228	0.2912	31.47
−Cl	38.13	0.0188	0.3738	62.08
−Br	66.86	0.0124	0.5799	76.6
−I	93.84	0.0148	0.9174	100.79
With rings				
$-CH_2-$	27.15	0.0116	0.1982	51.64
>CH−	21.78	0.0081	0.1773	30.56
=CH−	26.73	0.0114	0.1693	42.55
>C<	21.32	−0.018	0.0139	17.62
=C<	31.01	0.0051	0.0955	31.28
−O−	31.22	0.0138	0.1371	17.41
−OH (phenol)	76.34	0.0291	0.0493	−17.44
>C=O	94.97	0.0343	0.2751	59.32
>NH	52.82	0.0244	0.0724	27.61
>N−	52.82	0.0063	0.0538	25.17
−N=	57.55	−0.0011	0.0559	42.15
Other groups				
−B	−24.56	0.0352	0.0348	22.45
−P	34.86	−0.0084	0.1776	67.01
$-SO_2$	147.24	−0.0563	−0.0606	112.19

Figure 2.20: Groups considered for Modified Lydersen–Joback–Reid method [23]

To assess the "consistency" of the projected properties, an estimation of the liquid densities for the ionic liquids was carried out using a comprehensive correlation method originally introduced by Valderrama [23, 24]. This generalized correlation relies solely on the normal boiling temperature, molecular weight, and critical properties, drawing from the foundational equation established by Spencer and Danner [25].

The equations are succinctly summarized as follows:

$$\rho_L = \frac{MP_c}{RT_c}\left[\frac{0.3445P_cV_c^{1.0135}}{RT_c}\right]^{\theta} \tag{2.19}$$

$$\theta = -\left[\frac{1+(1-T_R)^{2/7}}{1+(1-T_{bR})^{2/7}}\right] \tag{2.20}$$

In these equations:

- P_L represents the liquid density in g/m^3.
- R stands for the ideal gas constant.
- T_R denotes the reduced temperature ($T_R = T/T_C$).
- T_{bR} signifies the reduced temperature at the normal boiling point ($T_{bR} = T_b/T_C$).

Another significant property to consider is the acentric factor, defined as:

$$\omega = -log\left(\frac{P^s}{P_c}\right)_{\left(\frac{T}{T_c}\right)=0.7} - 1 \tag{2.21}$$

The acentric factor, denoted as ω, represents a crucial numerical parameter that was first introduced by the chemist Kenneth Pitzer in the year 1955. Pitzer's groundbreaking contribution to the field of fluid dynamics gave rise to a profound conceptual tool that has since proven invaluable in the comprehensive characterization of fluids. This parameter has since emerged as a pivotal standard in the realm of thermodynamics and is wielded with precision in the description of single, pure chemical components.

In the landscape of fluid properties, the acentric factor sits alongside other essential parameters for describing the state, such as molecular weight, critical temperature, critical pressure, and critical volume (also known as critical compressibility). Together, these parameters form an essential toolkit for scientists and engineers engaged in the investigation and manipulation of fluid behaviour, whether in the confines of a laboratory or in the design of industrial processes.

The acentric factor ω is an indicator of the non-sphericity, or centricity, of molecular structures within a given fluid.

A key insight is that the shape of molecules plays a fundamental role in determining their thermodynamic behaviour. An increase in ω indicates a departure from sphericity and this deviation is reflected in the behaviour of the vapour-liquid equilibrium phase. In essence, the vapour curve, which represents the boundary between the liquid and vapour states, is 'pulled' downwards as the acentric factor increases. This shift in the vapour curve leads to the manifestation of higher boiling points for the fluid in question.

In this way, the acentric factor becomes a quantifiable measure of how far the shape of a molecule deviates from the idealised spherical shape, and this departure has significant implications for the physical properties and behaviour of the substance in both liquid and vapour states.

The utility of the acentric factor in the study of fluids therefore goes beyond mere mathematical abstraction; it has practical and tangible applications that allow us to predict and understand the phase behaviour of pure components.

The saturation pressure, denoted as P_s, at a reduced temperature of $T/T_C = 0.7$, was determined by a method based on several key parameters. This estimation method uses the temperature and pressure values of the critical point, represented by (P_c, T_c), as well as the values observed at the normal boiling point, indicated by (P_b, T_b). It also considers the vapour pressure relationship described by Rudkin [26] as a fundamental part of his calculations.

This approach provides an effective means of predicting saturation pressure under specific conditions, facilitating a deeper understanding of the thermodynamic behaviour of the substance in question.

In this particular methodology, water serves as the reference fluid, and the relationship between vapor pressure (P_s) and temperature (T) is established through the application of the Antoine equation.

Rudkin specifically employs a value of C, set at 43 when temperatures are expressed in Kelvin, which corresponds to water, the chosen reference fluid.

The equation used to calculate the saturation pressure adheres to the classical Antoine Equation, which consists of three fundamental parameters, denoted as A, B, and C.

By substituting the Antoine equation into the acentric factor definition, the final equation is revealed as follows:

$$\omega = \frac{(T_b-43)(T_c-43)}{(T_c-T_b)(0.7T_c-43)} log\left[\frac{P_c}{P_b}\right] - \frac{(T_c-43)}{(T_c-T_b)} log\left[\frac{P_c}{P_b}\right] + log\left[\frac{P_c}{P_b}\right] - 1 \qquad (2.22)$$

2.9.3 Combining and mixing rules

After the determination of the critical properties of the individual pure components that make up the deep eutectic solvents outlined in the context of this study, the next step involves the definition of mixing and combination rules. This imperative step is necessary because we are dealing with a combination of two or more chemical components, each of which possesses a unique set of physical and chemical attributes.

In this multifaceted realm of mixtures, the principles of mixing and combining are central. The term "combining rules," or often referred to simply as "combination rules," alludes to a set of mathematical expressions or equations that are instrumental in quantifying the interaction energies between dissimilar non-bonded atoms. These rules primarily concern the segment of the potential energy function that characterizes the van der Waals interactions between these atoms.

In essence, these combination rules bridge the gap between distinct components, providing a systematic means to calculate and understand the intermolecular forces at play. They encapsulate how different molecules interact with each other within a mixture, considering factors such as molecular size, shape, and the attractive and repulsive forces between particles.

These rules are therefore indispensable tools for understanding and predicting the behaviour of complex mixtures such as deep eutectic solvents, where the interaction of various molecular species requires a comprehensive framework to describe the forces at play. Consequently, their application is crucial in the broader field of thermodynamics and molecular modelling.

Within the scope of this investigation, the critical properties of the mixture are derived from the critical properties of the individual pure compounds through the application of Lee-Kesler mixing rules. The equations encapsulating this methodology are presented as follows:

$$T_{cm} = \frac{1}{V_{cm}^{1/4}} \sum_i \sum_j y_i y_j \, V_{cij}^{1/4} T_{cij} \qquad (2.23)$$

$$V_{cm} = \sum_i \sum_j y_i y_j \, V_{cij} \qquad (2.24)$$

$$\omega_m = \sum_i y_i \, \omega_i \qquad (2.25)$$

$$T_{cij} = (T_{ci} T_{cj})^{\frac{1}{2}} k'_{ij} \qquad (2.26)$$

$$V_{cij} = \frac{1}{8}\left(V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}\right)^3 \qquad (2.27)$$

$$P_{cm} = (0.2905 - 0.085)\omega_m \frac{RT_{cm}}{V_{cm}} \qquad (2.28)$$

In the context of these equations, there are several key components to consider:

1. **Subscript Notation:**

- The subscript "m" pertains to the mixture under investigation.
- Subscripts "i" and "j" correspond to the individual pure constituents within the mixture.
- The variable "y" represents the mole fraction of a particular pure constituent, either "i" or "j".

2. **Binary Parameters - *k'il*:**

- The binary parameters, denoted as "*k'il*", are crucial factors in these equations. These parameters play a pivotal role in quantifying the interactions between the different constituents in the mixture.
- It is noteworthy to mention that, as per the available information [11], these binary parameters are approximated to have a simplified unit value.
- This simplification stems from the absence of published data or specific values for these parameters, necessitating this convenient assumption.

The utilization of these equations and the incorporation of these parameters enable the calculation of critical properties for the mixture based on the known properties of the pure constituents. This approach proves invaluable in the field of thermodynamics and fluid dynamics, particularly when detailed data for binary interactions are unavailable, thus facilitating the comprehensive characterization of complex mixtures and their behaviour.

The table enumerating critical properties has been incorporated into the "Results and Discussion" chapter.

Chapter 3

Results and Discussion

In this section, we comprehensively analyse and detail the results obtained within this study. The chapter is divided into two sections: the first pertaining to the absorption and characterization results of the various studied DES, and the second part focusing on the outcomes arising from the electroreduction of the CO_2 absorbed within the DES.

3.1 CO_2 absorption results

3.1.1 *Chemical Absorption*

The solubility of carbon dioxide (CO_2) in various deep eutectic solvents (DESs) has been investigated at a temperature of 298.15 K and pressures reaching up to 2 MPa. These solubility values, expressed in terms of mole fraction and CO_2 loading, are thoughtfully catalogued in the table and figure provided below for reference and analysis.
In Figure 2, we are presented with a graphical representation of three distinct DESs:

- Im-MEA (1:2).
- Im-PEHA (1:2).
- Im-DEA (1:2).

These three DESs share a common hydrogen bond acceptor (HBA), but they differ in terms of their hydrogen bond donors (HBDs).
This selection of DESs for examination is of particular significance as it allows us to explore how the varying chemical compositions impact the absorption capacity of these solvents as the temperature gradually rises, reaching pressures of up to 2 MPa.
The data reveals a compelling trend: as the pressure within the reactor increases, the solubility of CO_2 in each respective DES experiences a notable upsurge. This finding underscores the critical role that pressure plays in modulating the interaction between CO_2 and DES, providing valuable insights for applications where CO_2 absorption and sequestration are essential considerations.
The isothermal diagram (P-x) revealed an interesting phenomenon within the deep eutectic solvents (DES) we studied. These solvents showed a particular departure from Rault's law, characterised by a discrete negative deviation. This observation strongly suggests the occurrence of chemical complex formation, a phenomenon that deserves further exploration.

In particular, this deviation suggests the intriguing prospect of interactions between the CO_2 molecule and the molecules that make up DES. These interactions are indicative of the formation of complexes, in which the CO_2 and DES molecules intertwine in chemical affinity. The revelation of the formation of such complexes is a noteworthy development, shedding light on the molecular-level interactions at play within these solvents and paving the way for deeper insights into their behaviour and potential applications.

The following graphs visually depict the CO2 absorption data for the three studied DES in both kg_{CO2}/kg_{DES} and Mol_{CO2}/Kg_{DES} bases.

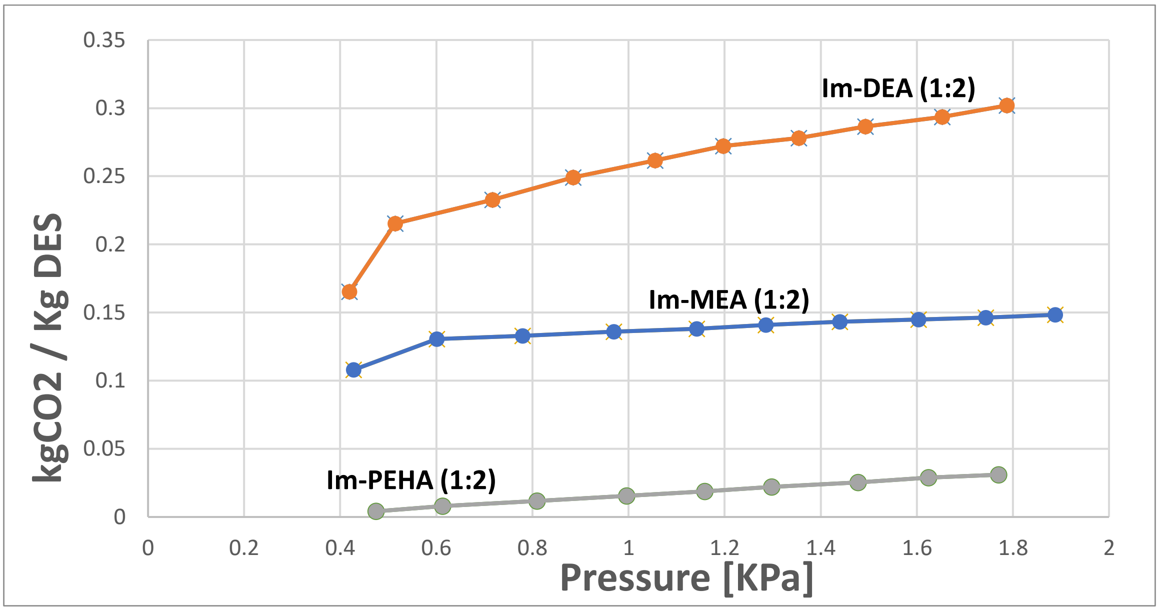


Figure 3.1: Absorption trend for different DES.

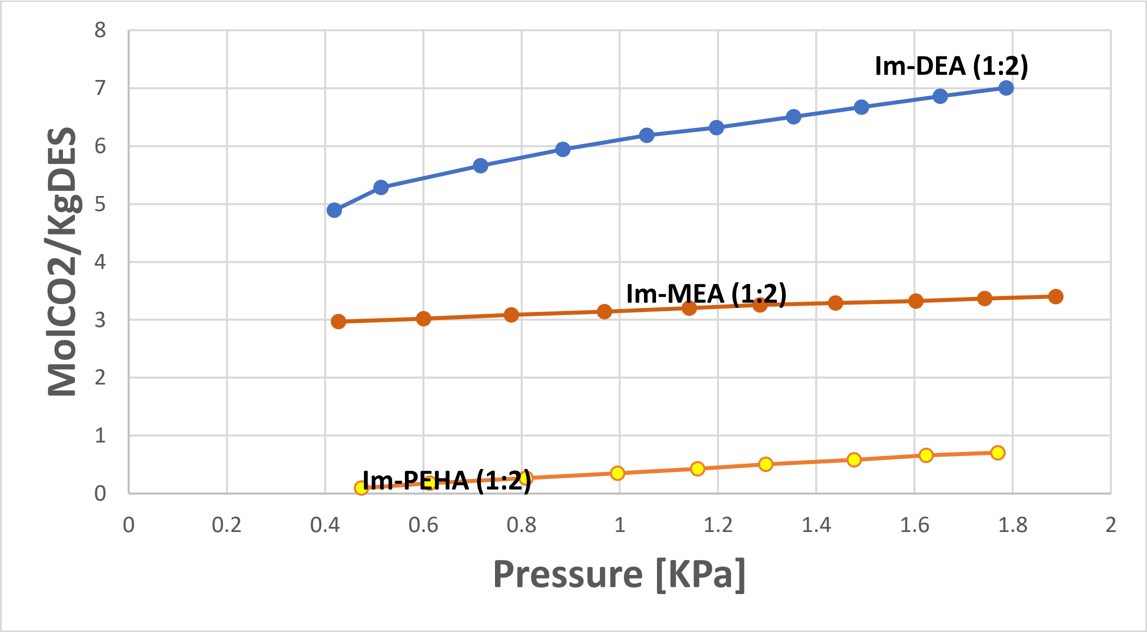


Figure 3.2: Absorption trend for different DES in Mol_{CO2}/kg_{DES}.

The table presented below offers a comprehensive overview of the maximum absorption capacities exhibited by the studied DES.

An analysis of the data within the table reveals that the first two DES stand out prominently due to their remarkable capability to absorb CO_2, signifying their exceptional performance in this regard.

Table 3.1: Maximum absorption values of DESs

DES	Im-MEA (1:2)	Im-DEA (1:2)	Im-PEHA (1:2)
Kg_{CO2}/KG_{DES}	0.148	0.301	0.031
mol_{CO2}/KG_{DES}	3.4024	7.0057	0.7064

The highest degree of CO_2 absorption is associated with the DES employing diethylamine as a constituent. Diethylamine possesses only one unoccupied hydrogen site available for hydrogen bond formation, and this distinctive feature is advantageous as it minimizes competition with other atoms for binding CO_2 molecules.

In contrast, pentaethylhexamine exhibits notably lower absorption values compared to the other two DES under scrutiny. This diminished absorption can be primarily attributed to the considerable elongation of its molecular chain. With a chain comprising 10 carbon atoms and 6 nitrogen atoms, pentaethylhexamine is five times longer than the chains present in diethylamine and monoethanolamine. The greater chain length results in a significantly higher molecular density compared to the other two examined Deep Eutectic Solvents. The table indicates an approximate tenfold increase for Monoethanolamine (MEA) and a fiftyfold increase for Diethylamine (DEA) in terms of density before and after CO_2 absorption, as highlighted in the second Chapter. This elevated density value poses a challenge for efficient CO_2 absorption, as the viscosity of DES plays a pivotal role in influencing the extent of CO_2 capture.

Another contributing factor to the lower absorption capacity is the presence of hydrogen atoms bonded to the internal amine groups within the molecule. These bonded hydrogens hinder the formation of bonds with CO_2 molecules, thus limiting their ability to interact effectively.

Furthermore, the CO_2 absorption attributed to diethylamine is characterized by stronger intermolecular hydrogen bonds in comparison to those associated with Monoethanolamine (MEA) or Pentaethylenehexamine (PEHA). This discrepancy in intermolecular bonding strength further influences the variations in CO_2 absorption observed between these DES.

The decrease in CO_2 absorption in Deep Eutectic Solvents as the length of the molecule's chain increases can be grouped as follows:

1. *Reduced Availability of Active Sites*: Longer chains in molecules like amines result in fewer available active sites for CO_2 absorption. Each amine group typically has a lone pair of electrons that can interact with CO_2 molecules to form hydrogen bonds. Longer chains have proportionally fewer of these amine groups, reducing the potential binding sites for CO_2.

2. *Hindered Molecular Movement*: Longer chain molecules are bulkier and more complex, leading to slower molecular movement within the solvent. Efficient CO_2 absorption depends on the rapid diffusion of CO_2 molecules into the solvent and their interaction with active sites. Longer chain molecules hinder this movement, reducing the rate of absorption.

3. *Increased Molecular Size*: Longer chain molecules have larger molecular sizes and, consequently, greater steric hindrance. This can limit the accessibility of CO_2 molecules to active sites on the molecule, making it more difficult for CO_2 to interact and be absorbed effectively.

4. *Weaker Solvent-Substrate Interactions*: Longer chains may result in weaker interactions between the solvent and CO_2 due to reduced proximity and steric hindrance. Weaker interactions lead to less effective CO_2 absorption.

5. *Enhanced Molecular Density*: Longer chains often result in a higher molecular density, which can lead to a decrease in the overall capacity of the solvent to absorb CO_2. While there are more potential binding sites in the longer molecule, they may not be as accessible or effective in capturing CO_2.

It's important to note that the specific behaviour of DES and the impact of chain length on CO_2 absorption can vary depending on the particular type of DES, the conditions of the absorption process, and the choice of solvents.

The procedures detailing the execution of the absorption tests within the reactor were elucidated in Chapter One. In this section, we present the data stemming from the diverse experiments conducted.

3.1.2 Im-MEA at different Molar Ratio

This section delves into the absorption tests conducted on three distinct Deep Eutectic Solvents (DES), all comprised of the same pure substances but featuring varying molar ratios. These DES are identified as follows:

- Im-MEA (1:2)
- Im-MEA (1:3)
- Im-MEA (1:4)

A comprehensive analysis of the data, as illustrated in the accompanying graph, reveals a notable trend: as the molar ratio of Monoethanolamine (MEA) is increased, the absorption of CO_2 exhibits a corresponding augmentation.

More specifically, the CO_2 absorption order is as follows: Im-MEA (1:2) < Im-MEA (1:3) < Im-MEA (1:4). This trend can be attributed to the reactivity of amines with CO_2, which follows the hierarchy: Primary > Secondary > Tertiary.

In this context, the introduction of a primary amine to the solution, even if it is the same amine present in the DES, results in elevated absorption values.

The increase in CO_2 absorption when you introduce a higher molar ratio of Monoethanolamine (MEA) into a Deep Eutectic Solvent (DES) formed by imidazole and MEA can be explained by the chemical properties of the components involved.

Monoethanolamine, being a primary amine, contains a primary amino group (NH2), which is more reactive with CO_2 than secondary or tertiary amines. This higher reactivity is due to the fact that primary amines have a free hydrogen atom on the nitrogen that can readily form a chemical bond with CO_2. This process is known as chemical absorption or chemisorption.

In a DES, the amine groups in MEA can act as sites for CO_2 absorption. When you increase the molar ratio of MEA in the DES, you are introducing more primary amine groups into the solution. As a result, there are more active sites available for CO_2 molecules to bind to, increasing the overall capacity of the solvent to absorb CO_2.

Additionally, the higher concentration of primary amine groups can lead to more efficient interactions between the solvent and CO_2 molecules, enhancing the absorption process.

In summary, increasing the molar ratio of Monoethanolamine in a DES formed by imidazole and MEA improves CO_2 absorption due to the higher reactivity of primary amines and the increase in available active sites for CO_2 binding.

The Figure 3.3 and the Figure 3.4 presents a comprehensive dataset depicting the values of CO_2 uptake and mole fraction within the three distinct Deep Eutectic Solvents (DES) under examination. This dataset offers a detailed snapshot of the absorption characteristics and the distribution of CO_2 within these DES, shedding light on their performance in capturing carbon dioxide.

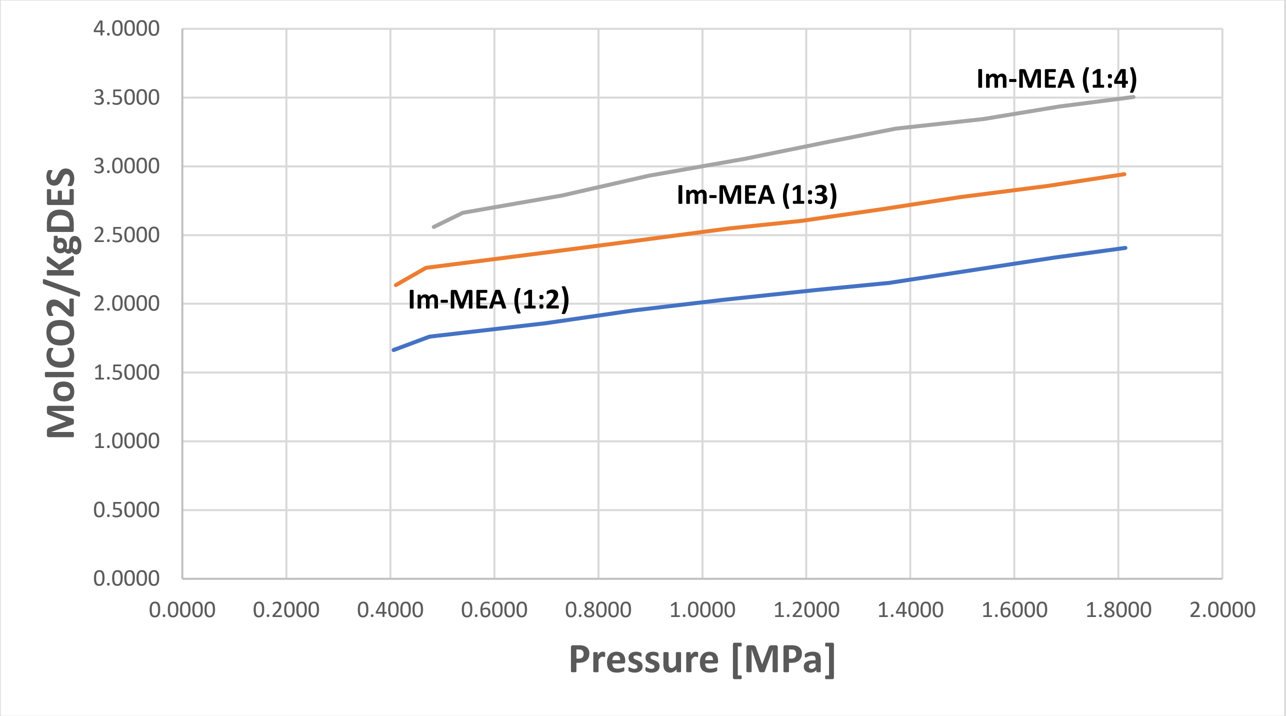


Figure 3.3: Absorption trend in the same DES but with different molar ratio in Mol$_{CO2}$*/Kg*$_{DES}$*.*

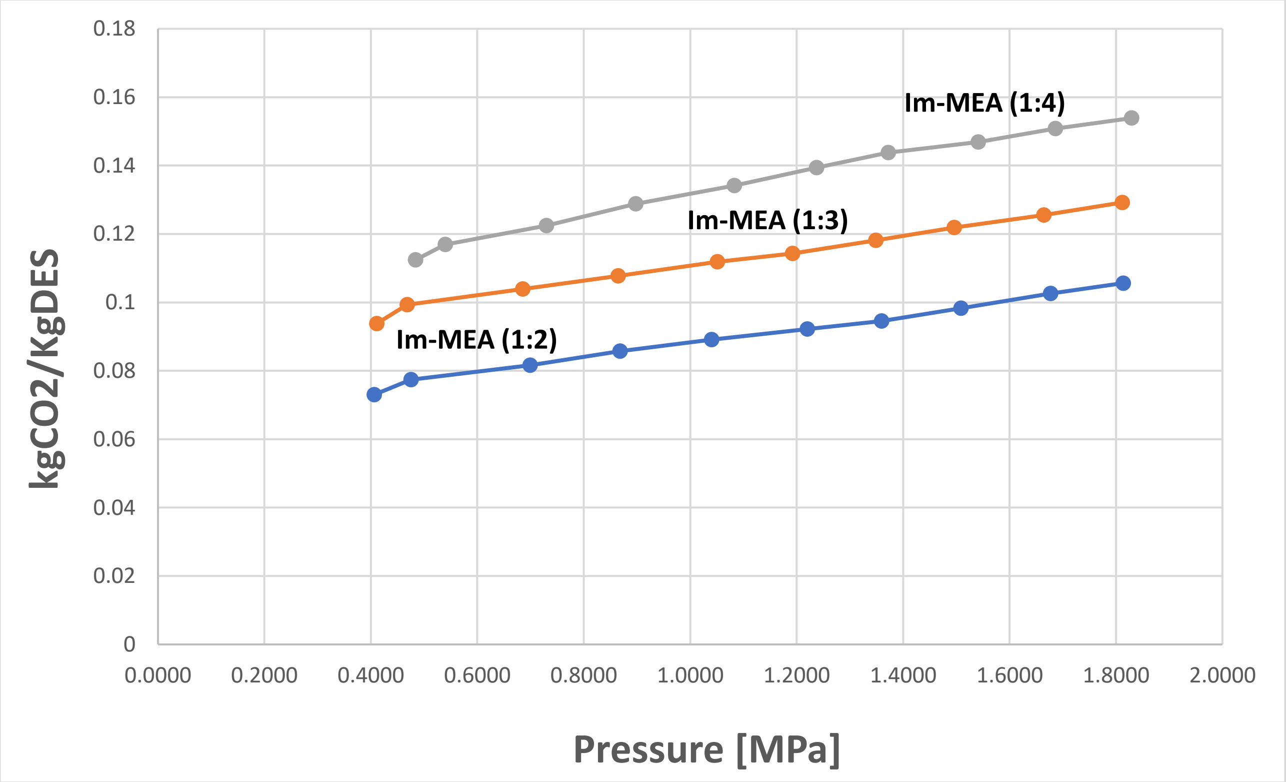


Figure 3.4: Absorption trend in the same DES but with different molar ratio in Kgl$_{CO2}$*/Kg*$_{DES}$*.*

3.1.3 Im-MEA at different molar ratio studied at different Temperature

In this particular section, the investigation delves into the carbon dioxide (CO_2) absorption capacity of DES composed of imidazole and MEA. The study involves a comprehensive examination of solvent performance at various molar ratios and temperature settings.

The experimental setup employed remains consistent with that used for room temperature conditions, with one notable exception: the temperature parameter. In order to fully understand the influence of temperature on CO_2 uptake, the temperature is changed, and increased each time while keeping the other factors constant.

The data obtained, together with the main results, are presented graphically in the next section, providing a visual representation of the CO_2 absorption characteristics of the solvent under different conditions. These graphical representations are crucial to facilitate understanding of the intricate relationship between the DES imidazole-MEA system, molar ratios, and temperature variations in CO_2 uptake.

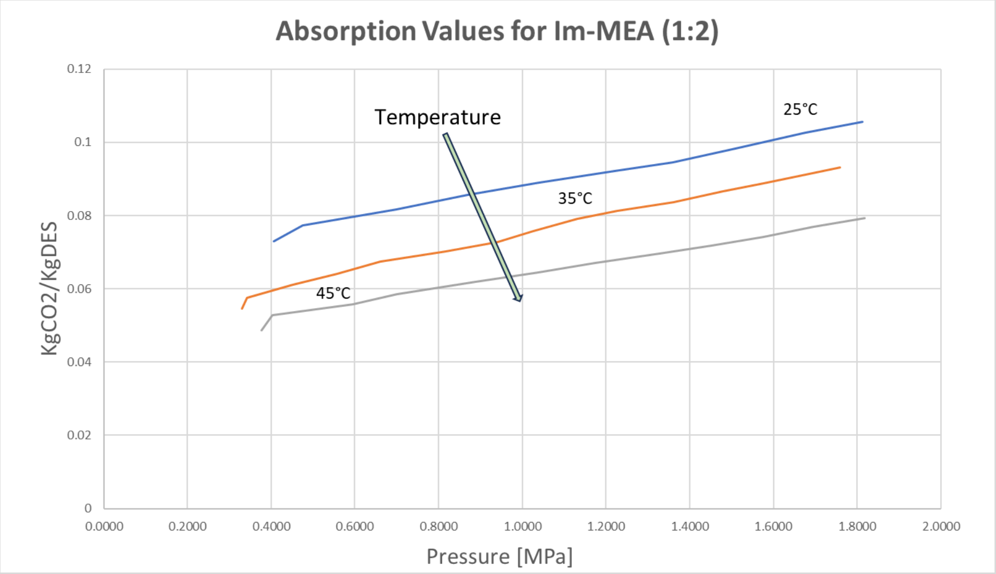


Figure 3.6: Absorption trend for Im-MEA (1:2) at different temperatures.

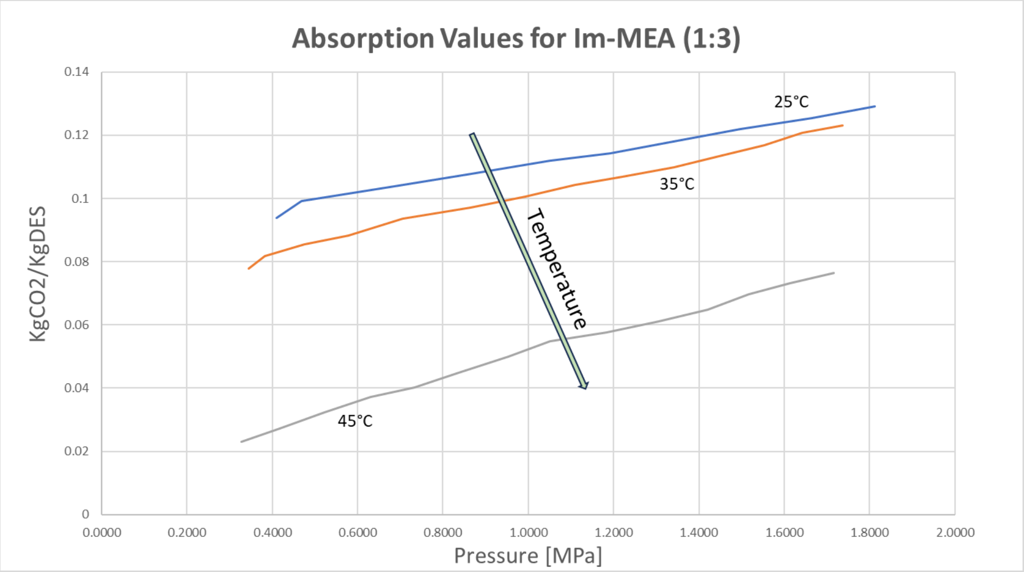


Figure 3.7: Absorption trend for Im-MEA (1:3) at different temperatures.

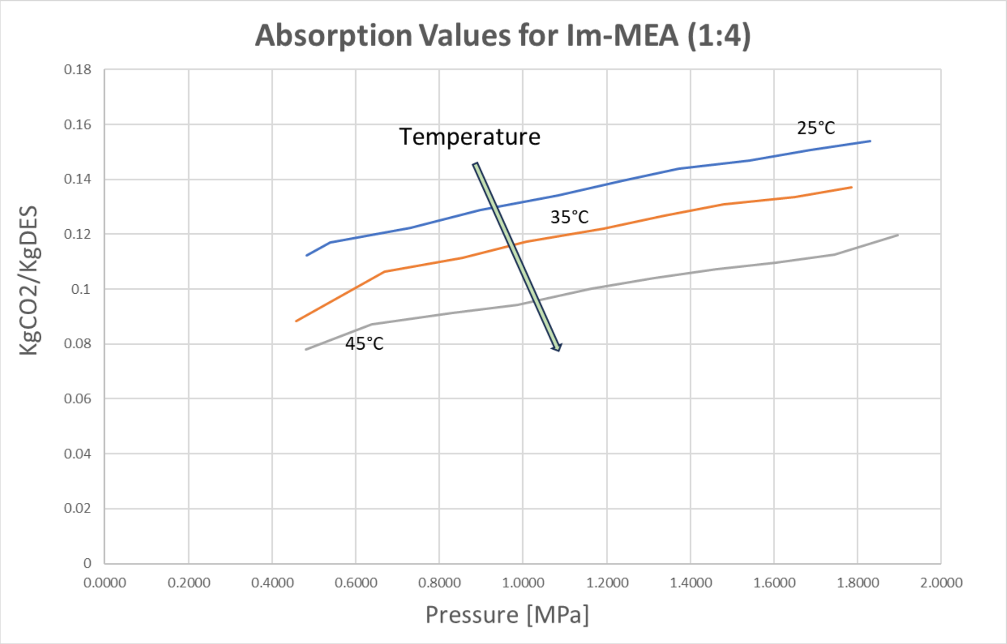


Figure 3.7: Absorption trend for Im-MEA (1:4) at different temperatures.

The decrease in CO_2 absorption when increasing the temperature in a deep eutectic solvent (DES) composed of Imidazole and Monoethanolamine (MEA) while keeping the molar ratio constant can be attributed to several interrelated factors:

1. *Thermodynamic Equilibrium*: The solubility of gases in a solvent typically decreases with increasing temperature due to the principles of thermodynamics. As the temperature rises, the equilibrium position for the reaction between CO_2 and the DES shifts in favor of CO_2 desorption, resulting in decreased absorption.

2. *Exothermic Nature of Absorption*: CO_2 absorption is often an exothermic process, meaning it releases heat during the absorption reaction. When the temperature is elevated, the energy balance is disrupted, and the absorption reaction becomes less favorable. This is due to the counteractive effect of the increased temperature, which competes with the exothermic heat release.

3. *Reduced Solvent Viscosity*: Higher temperatures can lead to a decrease in the viscosity of the DES. Lower viscosity can reduce the interaction between CO_2 molecules and the solvent, making it less effective at capturing and retaining CO_2.

4. *Enhanced CO_2 Desorption*: Higher temperatures accelerate the desorption of CO_2 from the solvent, as it reduces the strength of the CO_2-solvent interactions. This can result in CO_2 molecules escaping from the solvent more easily, leading to reduced absorption efficiency.

5. *Shift in Chemical Equilibria*: The chemical equilibria within the DES system may be affected by temperature changes. As temperature increases, it can alter the balance of reactions and the species present in the solution, affecting the overall CO_2 absorption capacity.

It's essential to consider that the specific behaviour of the DES system under different temperature conditions may vary depending on the composition, concentration, and the characteristics of the DES. In practice, the design and optimization of DES-based CO_2 capture processes must carefully balance factors like temperature, pressure, and molar ratios to achieve optimal CO_2 absorption efficiency.

3.1.4 Physical Absorption

In this particular section of our research, we delve into the realm of carbon dioxide (CO_2) absorption within deep eutectic solvents specifically formulated to examine physical absorption. As explained in the previous section, the phenomenon of physical absorption is predominantly based on relatively weaker intermolecular forces, which gives it the distinctive characteristic of having a relatively short duration.

For this specific phenomenon, our main source of evidence is the act of absorption occurring exclusively within the confines of our reactor. This single measurement serves as an indicator to quantify the absorption strength of these specialised solvents. All other conventional characterisation techniques, such as Fourier transform infrared spectroscopy (FTIR), viscosimeter, nuclear magnetic resonance (NMR) or gas chromatography-mass spectrometry (GC-MS), unfortunately remain inapplicable due to the inherent volatility of the absorption process.

In this comprehensive study, we undertook the analysis of two distinct deep eutectic solvents:

1. TPAB - formic acid
2. TPAB - acetic acid

These solvents were formed through a standardised procedure.
It is important to note that these solvents were examined for their chemical adsorption potential.
The graphs that follow in this section correspond to classic adsorption tests analysed in the course of our research. These tests were conducted under controlled conditions, with the temperature kept constant at 25 degrees Celsius and the pressure gradually increased to 2 megapascals (MPa).

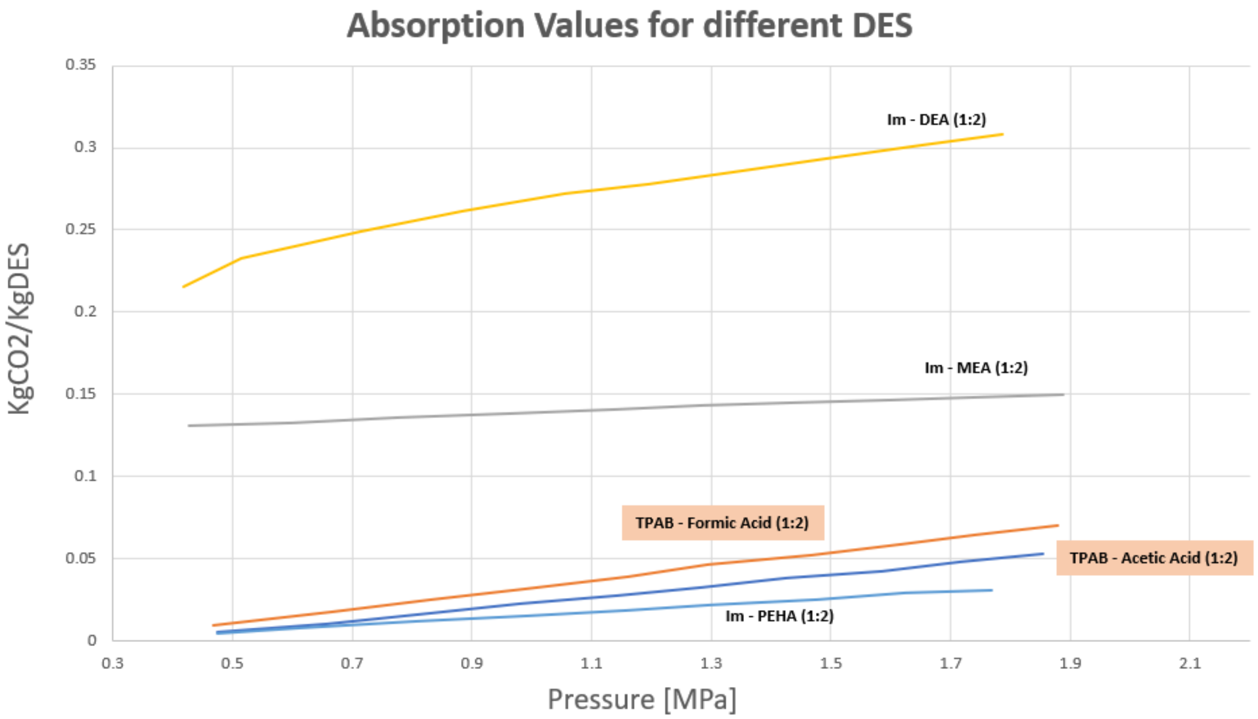


Figure 3.7: Comparison of DES absorption trends for chemical and physical absorption

Upon an examination of the data presented in these graphical representations, a discernible pattern emerges. It becomes evident that the absorption values attributed to the two deep eutectic solvents under scrutiny exhibit a noteworthy characteristic: they are notably modest, surpassing only the least effective performers among the DES compounds crafted specifically for chemical absorption.
This observation underscores a crucial aspect of our investigation, shedding light on the intrinsic disparities between DES designed for physical absorption and their counterparts tailored for chemical absorption.
The disparity in CO_2 absorbance between deep eutectic solvents (DES) designed for physical absorption and those tailored for chemical absorption can be attributed to the fundamental differences in the underlying mechanisms and properties of these two types of solvents. Let's explore the key factors that contribute to this discrepancy:

1**.** *Dissimilar Mechanisms:*

- Physical Absorption: In DES formulated for physical absorption, the primary mode of CO_2 capture is through weak intermolecular forces such as van der Waals forces and dipole-dipole interactions. These forces are relatively weaker and less specific, resulting in a limited capacity for CO_2 absorption. Additionally, physical absorption is typically reversible, making it less efficient for long-term CO_2 capture.

- Chemical Absorption: DES designed for chemical absorption are specifically engineered to chemically react with CO_2. This chemical reaction leads to the formation of chemical compounds (e.g., salts) with CO_2, which can greatly enhance the CO_2 absorbance capacity. Chemical absorption is often more robust and can provide a higher CO_2 loading capacity compared to physical absorption.

2. *Selectivity:*

DES designed for chemical absorption can be tailored to exhibit higher selectivity for CO_2 over other gases present in the environment. This selectivity ensures that CO_2 is preferentially captured, leading to higher absorption efficiency.

3. *Reaction Kinetics:*

Chemical absorption reactions in DES can occur relatively quickly, leading to faster CO_2 capture. In contrast, physical absorption processes, based on weak intermolecular forces, take longer to achieve the same level of CO_2 absorption.

4. *Regeneration Efficiency:*

DES used for physical absorption may allow for easier regeneration by reducing the energy required to release the absorbed CO_2. On the other hand, DES designed for chemical absorption may require more energy-intensive regeneration processes due to the chemical reactions involved.

In summary, DES formulated for physical absorption have inherently limited CO_2 absorbance due to the weaker intermolecular forces and the absence of chemical reactions that enhance capture efficiency. DES for chemical absorption, on the other hand, are specifically tailored to chemically react with CO_2, resulting in higher absorbance capacity and selectivity. However, the choice between physical and chemical absorption depends on the specific requirements of the application, including the need for selectivity, regeneration efficiency, and the nature of the gases to be captured.

3.1.5 Critical Properties for the studied DES

This section presents a comprehensive analysis of the critical properties that were studied using the methodologies outlined in Chapter 2. It provides a detailed account of the results, offering insights into the critical aspects of the data obtained from the application of the various techniques and procedures described above.

The table below catalogues the critical properties that are the focus of this report.

Table 3.2: Critical Properties for the studied DES

DES	T_{BM}	T_C	P_C	V_{CM}	ρ_L	ω
Chemical Absorption						
Im-MEA (1:2)	403.0377	601.7323	30.70528	201.6852	1.3487	0.602368
Im-DEA (1:2)	356.9551	547.7069	11.04159	288.5211	1.301808	0.340439
Im-PEHA (1:2)	646.9646	862.8768	18.86246	688.0575	0.890737	0.880344
Physical Absorption						
TPAB-Formic Acid (1:2)	426.2972	588.0537	15.47924	302.942	1.593655	0.466735
TPAB-Acetic Acid (1:2)	457.3249	630.1398	12.85301	355.1266	1.421598	0.423964

Critical properties are paramount in the characterization of deep eutectic solvents because they provide fundamental information about the chemical and physical behaviour of these solvents.

Thermal stability is a prime example, where a full understanding of thermal attributes, such as melting point and decomposition temperature, is imperative. These properties are not merely academic: they define the operating temperature range of DES, thus dictating its viability and stability under various conditions.

Similarly, the dissolution capacity of a DES is a key parameter. The solvent's ability to dissolve various solutes - quantified and qualified by its solvation properties - is a cornerstone for its use in various applications, from extraction processes to the intricate realms of electrochemistry and chemical synthesis. The solvation properties mean that DES can serve as a versatile medium for chemical reactions, separation processes and even as a medium in electrochemical cells.

Furthermore, the density and viscosity of a DES are properties that speak volumes about its physical behaviour and its interaction with other substances. The viscosity of a DES influences its flow behaviour. Density, on the other hand, plays a key role in separation techniques.

In essence, the critical properties of DESs are the determinants of their compatibility and performance in various chemical processes.

The acentric factor is a significant parameter in the characterization of deep eutectic solvents because it provides a measure of the deviation of a substance's behaviour from that of an ideal gas.

In the context of DESs, the importance of the acentric factor can be detailed as follows:

1. *Predictive Power:* It aids in the prediction of thermodynamic properties, such as vapor pressure and boiling point, which are crucial for process design and understanding the volatility of DESs.

2. *Molecular Interaction Insight:* The acentric factor gives insight into the molecular interactions within the DES. A higher value generally indicates stronger deviations due to stronger intermolecular forces, such as hydrogen bonding, which is a key interaction in DESs.

3. *Solvent Selection:* When choosing a DES for a particular application, the acentric factor can help in selecting solvents with the desired volatility and solvation properties.

4. *Phase Equilibrium Calculations:* In separation processes involving DESs, the acentric factor is used in equations of state to calculate phase equilibria.

One key aspect of this analysis is the possibility of estimating compound density at room temperature based on the density determined under critical conditions, calculated using mathematical formulas. The following graph illustrates the comparison between the density evaluated at a temperature of 25 degrees and that evaluated under critical conditions. As evident from the graph, the difference is marginal, suggesting that this value can serve as an initial point for estimating density.

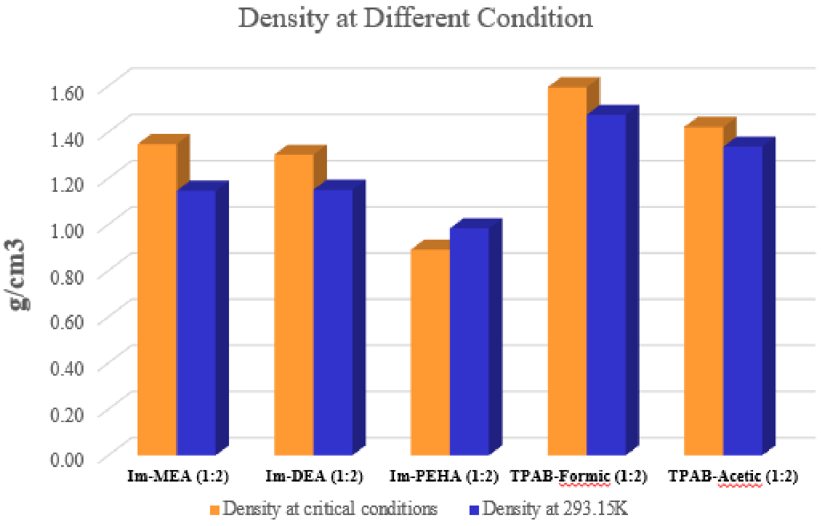


Figure 3.8: Density comparison between 25 °C and at critical condition

3.1.6 RETM Results

This part of the thesis delves into a complete analysis of the results obtained from the implementation of the RETM equation. An in-depth exposition of the meaning of the equation and its fundamental principles has been extensively outlined in a dedicated context of the second chapter.

In this current step, the focus shifts to an elucidation of the graphical data and the resulting results. The goal is to provide a nuanced understanding of the implications and practical applications that arise from the equation, highlighting the complexities observed in the pattern of results and their relevance to the broader field of study.

The resolution of this equation is facilitated by the utilization of MatLab, which employs a fitting algorithm to integrate known variables like P and m_{RNH20} with the unknown parameters, specifically H, K_1, and K_2. This computational approach allows for the determination of the quantities of CO_2 absorbed through both chemical and physical processes. By aligning the data points with the theoretical model, the software adeptly distinguishes between the chemical and physical absorption rates, yielding a comprehensive analysis of the CO_2 absorption dynamics.

Below is the graphical depiction of the results for the equation as applied to the sample of Imidazole-MEA (1:2).

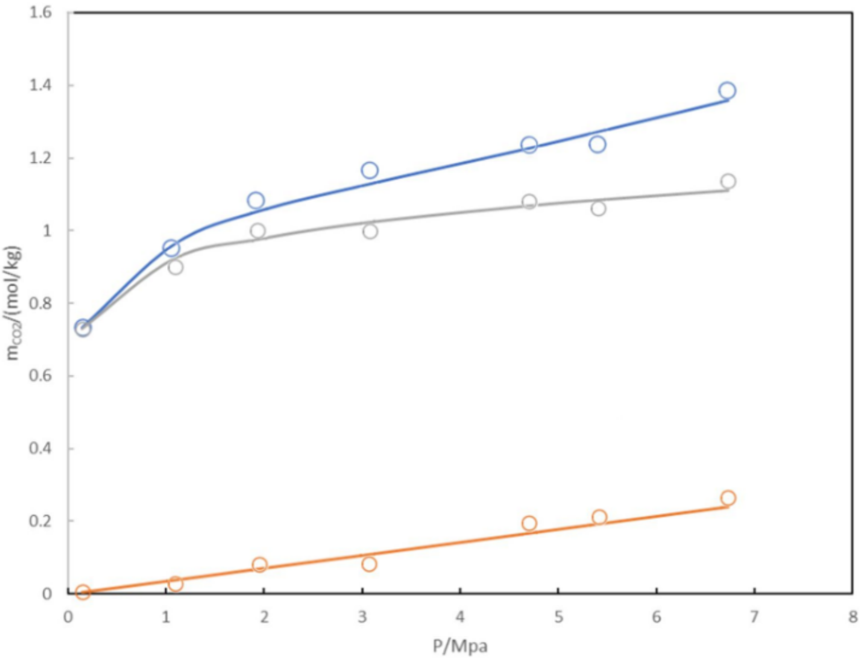


Figure 3.9: Physical and chemical solubility of CO_2 in Im-MEA (1:2) at 293.15K.

- The graph includes a lower curve, depicted in orange, which illustrates the quantity of CO_2 physically absorbed. This curve is characterized by a constant slope of 0.0479, indicating a direct and proportional relationship between pressure and CO_2 capture. The linear progression of this trend corroborates the underlying equation governing physical absorption, which adheres to the classic linear formula ($y = mx + c$). In this instance, 'm' (the slope of the line) has a value of 0.0479, reflecting the rate of increase in CO_2 absorption with pressure, while 'c' (the y-intercept) is equal to 0. This demonstrates that at the starting point, when the pressure is at its initial state, the absorbed amount of CO_2 is zero. As pressure escalates, the volume of CO_2 absorbed rises in a predictable and straight-line fashion, which can be precisely anticipated using the given linear equation. This visual and mathematical analysis allows for a clear understanding of the absorption behaviour of the Imidazole-MEA (1:2) sample under varying pressure conditions.

- The graph features an intermediate curve that signifies the chemical absorption of CO_2. Unlike the lower curve, which exhibits a linear trend, this middle curve presents a distinctly non-linear pattern. This non-linearity is evident upon examination of the graphical data, where the curve's trajectory deviates from a straight line, suggesting a more complex relationship between the variables at play. This complexity is characteristic of chemical absorption processes, which are often governed by a set of reactions that do not adhere to simple proportionality. The shape of the curve reflects the kinetics of the chemical interactions involved in the absorption process, where factors such as reaction rates, equilibrium states, and saturation limits come into play. Understanding the nuances of this curve is essential for interpreting the behaviour of chemical absorption in the given context, as it provides insights into how changes in certain conditions can significantly affect the amount of CO_2 that is chemically sequestered.

- Positioned at the pinnacle of the graph, the uppermost curve encapsulates the aggregate of physical and chemical absorption, thus representing the total CO_2 uptake by the designated deep eutectic solvent (DES). A closer inspection of the graph reveals that, with the exception of the initial segment, the trajectory of this composite curve largely follows a linear path. The slope of this linear progression, quantified by a specific value 0.3667, indicates the rate at which the total CO_2 uptake increases as the conditions—such as pressure or concentration—change. The onset of this uppermost curve is aligned with the beginning of the chemical absorption curve, signifying that at this initial juncture, the contribution of physical absorption to the total CO_2 uptake is negligible, effectively zero. This concurrence is logical since physical absorption often requires a certain threshold to overcome inertia before it commences, whereas chemical absorption begins immediately under the right reactive conditions.

  As the graph progresses beyond this initial point, the total uptake curve begins to climb steadily, mirroring the increase in CO_2 absorption due to both physical and chemical processes. The linearity of the curve beyond the first point suggests a consistent, predictable increase in total CO_2 uptake, which could be instrumental for industrial applications where maintaining specific absorption rates is crucial. This curve is a tool for visualizing and quantifying the overall efficiency of the CO_2 absorption process within the studied DES, offering a clear and integrated perspective of the system's performance.

The graphical representation not only serves to delineate the three distinct absorption curves, but also plays a critical role in the computational determination of three unknown critical parameters through a fitting process. These parameters include Henry's constant, which is integral to quantifying the extent of physical adsorption, and the two kinetic constants that govern the rate and capacity of chemical adsorption.

Henry's constant reflects the solubility of CO_2 in the solvent, and its value is indicative of how quickly the gas is absorbed under a given set of conditions. The two kinetic constants for chemical sorption are essential to understanding the dynamics of the reaction.

The calculated values of Henry's constant and the two kinetic constants are critical; they not only provide deeper insight into the fundamental properties of the sorption system, but also allow fine-tuning of the process for greater efficiency. These values, meticulously calculated, are reported below:

1. $H = 28$ [MPa^{-1}]
2. $K_1 = 1.32$
3. $K_2 = 29.03$

The outcomes presented here shed light on the kinetic behaviours of the absorption process, with a particular emphasis on the second kinetic constant. This constant pertains to the reaction kinetics involving two molecules of the deep eutectic solvent (DES) interacting with a single molecule of CO_2. The data indicates that this reaction sequence is characterized by a relatively higher rate constant compared to other reactions in the system, which implies a more rapid progression towards the formation of the resultant compound. The enhanced rate signified by the larger value of the second kinetic constant suggests that the reaction between the two DES molecules and CO_2 is not only faster but also more thermodynamically favoured under the conditions studied. This implies a higher probability of occurrence and efficiency in the absorption process, pointing to a significant affinity between the reactants. A kinetic constant of greater magnitude typically reflects a reaction pathway with lower activation energy or a higher transition state probability, signifying that the system can attain equilibrium more swiftly. This kinetic advantage could be attributed to the intrinsic properties of the DES, the physical conditions under the study, or a combination of both, contributing to a more favourable interaction with CO_2 molecules.

By understanding the kinetic profiles of these reactions, it is possible to engineer DES with tailored properties that maximize CO_2 uptake rates, thereby enhancing the overall efficiency and effectiveness of the absorption process.

The Henry's Law constant, often represented as H, relates the concentration of a gas in a liquid to the partial pressure of that gas above the liquid. A Henry's Law constant value of 28 MPa^{-1} means that for every megapascal (MPa) increase in the partial pressure of CO_2 above the solvent, the concentration of dissolved CO_2 in the solvent increases by 28 times the concentration that would be present at a partial pressure of 1 MPa, assuming ideal behaviour. In practical terms, a high value of the Henry constant, such as 28 MPa^-1, indicates that the gas (in this case, CO_2) is relatively soluble in the solvent. It suggests that as the pressure of CO_2 increases, the amount dissolved in the liquid will be significant. This is useful in applications such as carbon capture where a high solubility of CO_2 in a solvent is desirable; the higher the value of the Henry's Law constant, the more effective the solvent will be at absorbing CO_2 at a given pressure.

However, it's important to note that real solutions do not always behave ideally, and the relationship between pressure and solubility can be affected by factors such as temperature, the nature of the solvent, the presence of other solutes, and the specific interactions between the molecules of the gas and the solvent.

3.2 Characterization Results

3.2.1 FTIR

The investigation of the carbon dioxide (CO_2) absorption mechanism within Deep Eutectic Solvents was conducted using Fourier Transform Infrared (FTIR) spectroscopy, a characterization method thoroughly elaborated in the dedicated section. In the ensuing discussion, we present the FTIR spectrum for the Imidazole-MEA (1:2) sample, illustrating the outcome of this initial experimental evaluation.

In this initial test, the study focused on the adsorption of CO_2 within a DES created through the combination of Imidazole and a primary amine, namely Monoethanolamine (MEA).

The FTIR spectrum exhibits two distinct lines: one in black, representing the sample prior to CO_2 absorption, and another in red, indicating the sample's state after CO_2 adsorption. This visual contrast allows us to discern significant changes brought about by CO_2 interaction within the DES.

Notably, after CO_2 absorption, two new peaks become evident within the FTIR spectrum, signifying the emergence of molecular complexes within the DES. These newly observed peaks are situated at specific wavenumbers:

- 1388 cm^{-1}, corresponding to the stretching vibration of the N-C=(O) bond within the carbamate functional group.
- 1164 cm^{-1}, signifying the stretching vibration of the (C-N) bond within the carbamate moiety.

The presence of these peaks after CO_2 absorption unequivocally demonstrates the formation of distinct complexes within the DES, providing tangible evidence of the successful completion of the experiment. This corroborates the efficacy of CO_2 absorption and attests to the DES's suitability for carbon capture and related applications.

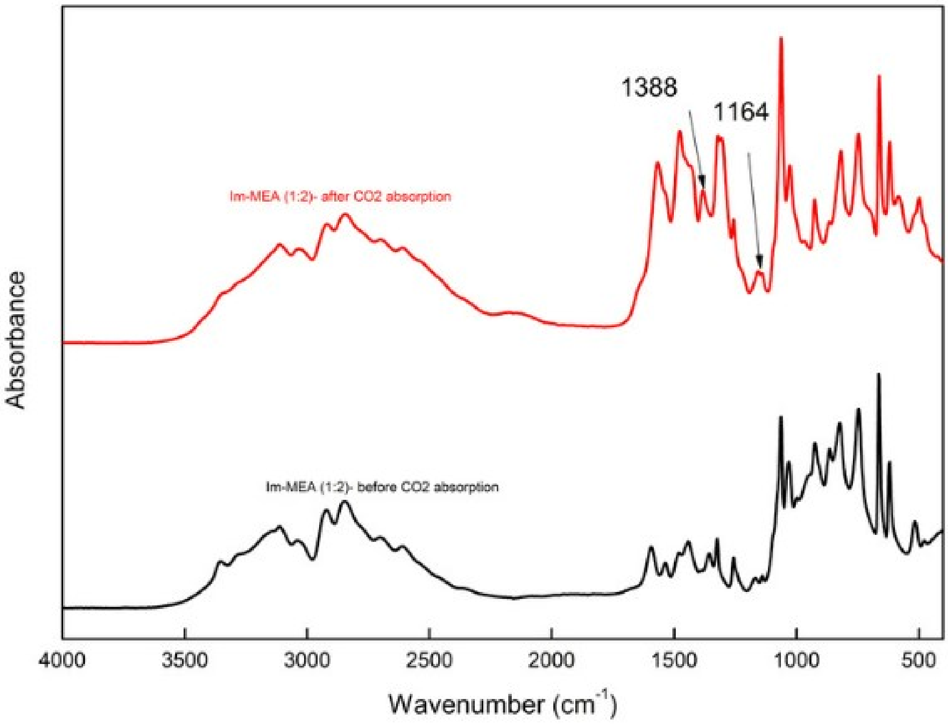


Figure 3.10: FTIR spectre for Im-MEA (1:2)

The FTIR spectrum of the second DES under investigation, Imidazole-Diethanolamine (Im-DEA) in a 1:2 molar ratio, is visually depicted in the graph below.

Similar to our previous examination, the FTIR spectrum of Im-DEA DES exhibits intriguing features following CO_2 adsorption. Here, we again observe the emergence of two distinctive peaks, which mark the occurrence of significant chemical changes within the DES following interaction with CO_2. These peaks are located at well-defined wavenumbers:

- At 1440 cm-1, a pronounced peak is observed, which can be attributed to the stretching vibration of the N-C=(O) bond within the carbamate functional group.
- Another prominent peak at 1290 cm-1 represents the stretching vibration of the (C-N) bond within the carbamate moiety.

The persistence of these two peaks after CO_2 absorption indicates the formation of complex molecular structures within the Im-DEA DES. This observation provides convincing evidence to support the effectiveness of the CO_2 adsorption process in this DES, reinforcing the idea that it has indeed undergone a successful adsorption test.

Furthermore, the appearance of these peaks highlights the potential usefulness of the Im-DEA DES in carbon capture applications, as the presence of CO_2-induced complexes attests to its ability to capture and sequester carbon dioxide. Detailed analysis of these spectral changes deepens our understanding of the chemical behaviour and capacity of this DES.

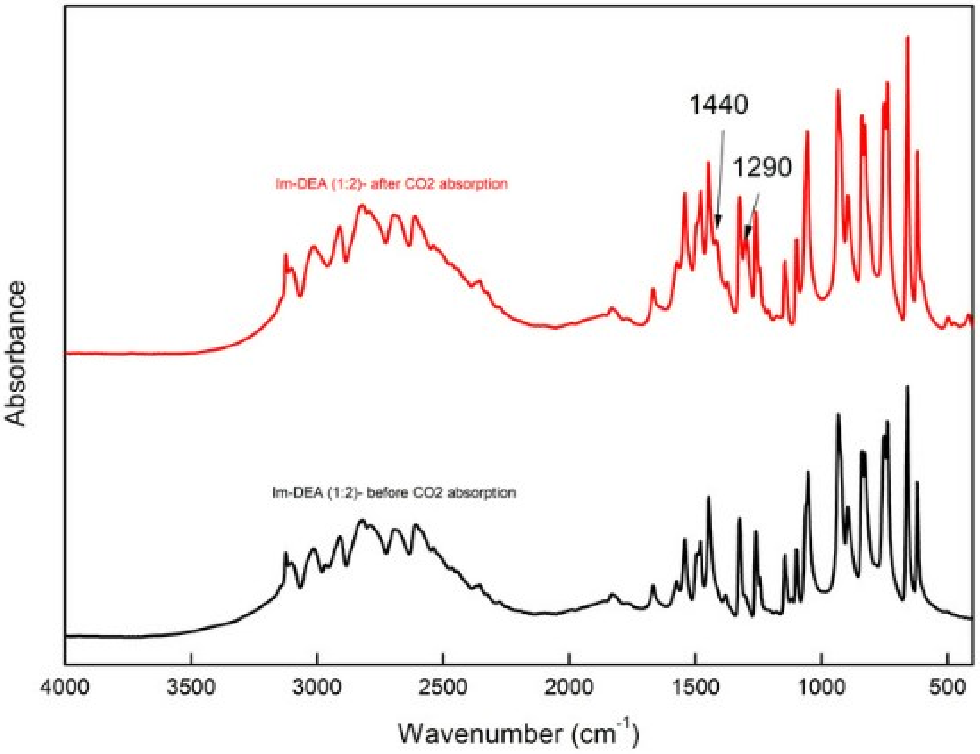


Figure 3.11: FTIR spectre for Im-DEA (1:2)

To continue our study, the same test procedure was employed to examine the third DES in question, called Imidazole- Pentaethylenehexamine (Im-PEHA), at a molar ratio of 1:2. In this particular analysis, an attempt was made to elucidate the CO_2 uptake behaviour within the Im-PEHA DES and to ascertain any noteworthy chemical changes induced by this interaction.

Contrary to the results observed in the previous tests, the results of the uptake tests with their curves reveal a surprisingly low degree of CO_2 uptake within the Im-PEHA DES. This result is further confirmed by a close examination of the FTIR spectrum, where a distinct absence of discernible peaks after CO_2 absorption is noted. This absence implies that the typical characteristic peaks that would indicate the formation of carbamate complexes do not visibly manifest themselves in the FTIR spectrum, emphasising the significantly limited extent of interaction with CO_2 within this DES.

While it is understood that complex formation occurs within the Im-PEHA DES, the current limitations of the FTIR analysis method prevent the direct visualisation of carbamate formation. Consequently, the absence of observable peaks in the FTIR spectrum after CO_2 uptake hampers our ability to directly infer carbamate formation through this analysis alone.

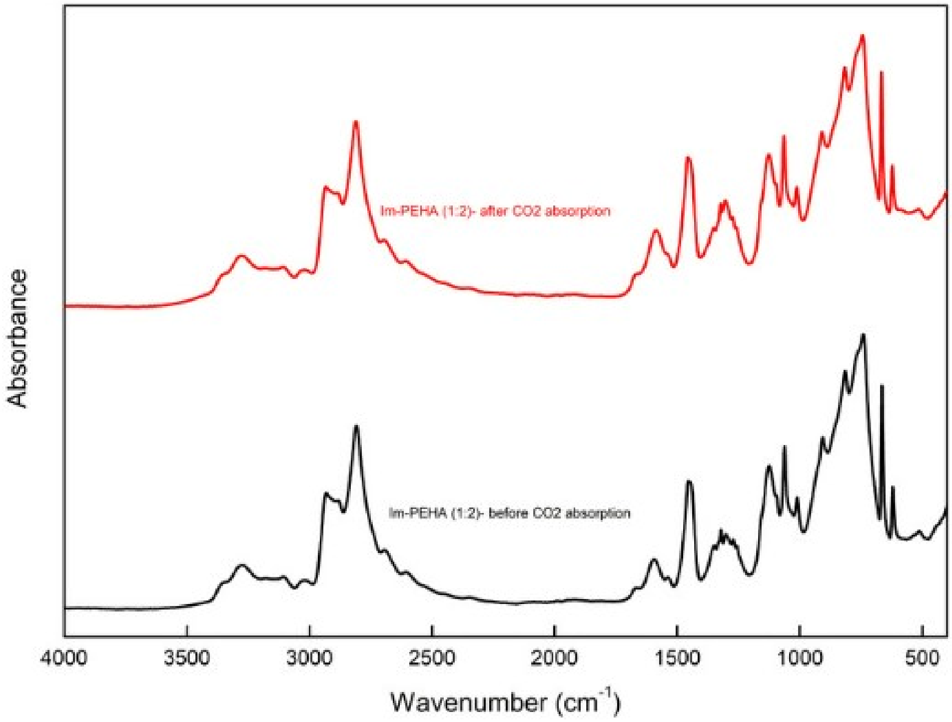


Figure 3.12: FTIR spectre for Im-PEHA (1:2)

The absence of a generic peak for carbamate formation in the FTIR spectrum of a deep eutectic solvent (DES) created with Imidazole and Pentaethylenehexamine (PEHA) can be attributed to several factors:

- *Concentration and Reactivity:* The concentration of carbamate or other reaction products may be lower in the Im-PEHA DES, which can result in reduced FTIR signal intensity. Additionally, the rate of carbamate formation may be slower in this DES, making it challenging to capture the reaction in real-time using FTIR.

- *Solvent Effects:* The nature of the solvent can affect the spectral features, potentially causing the carbamate peak to be less prominent or shifted in the spectrum.

- *Experimental Conditions:* Variations in experimental conditions, such as temperature, pressure, and reaction time, can affect the reaction kinetics and the extent of carbamate formation, which, in turn, impacts the FTIR results.

- *Sensitivity of the FTIR:* The sensitivity and resolution of the FTIR instrument used in the analysis may not be sufficient to detect subtle peaks associated with carbamate formation in the Im-PEHA DES.

To gain a deeper understanding of the carbamate formation in the Im-PEHA DES, further investigations using complementary analytical techniques and more precise experimental conditions may be required. These could include NMR spectroscopy or mass spectrometry which might provide more detailed insights into the chemical reactions occurring within this particular DES.

3.2.2 NMR

The investigation into the intricate mechanism of carbon dioxide (CO_2) absorption in Deep Eutectic Solvents (DESs) was pursued using the advanced technique of Nuclear Magnetic Resonance (NMR) spectroscopy. Comprehensive assessments were conducted, encompassing both Carbon-13 NMR (C-NMR) and Hydrogen-1 NMR (H-NMR) analyses.

Presented below are the results of this extensive study, accompanied by the detailed illustrations that portray the intricate dynamics at play.

The initial focus was on scrutinizing the behaviour of the DES named Im-MEA (1:2). Delving into the insights provided by the C-NMR graph, a prominent emergence of a peak at approximately 165 parts per million (ppm) was unequivocally observed, confirming the presence of carbamate within the system. While prior examinations employing Fourier-transform infrared spectroscopy (FTIR) hinted at this phenomenon, the application of NMR spectroscopy undeniably reinforced this critical observation, offering a deeper understanding of the underlying molecular interactions.

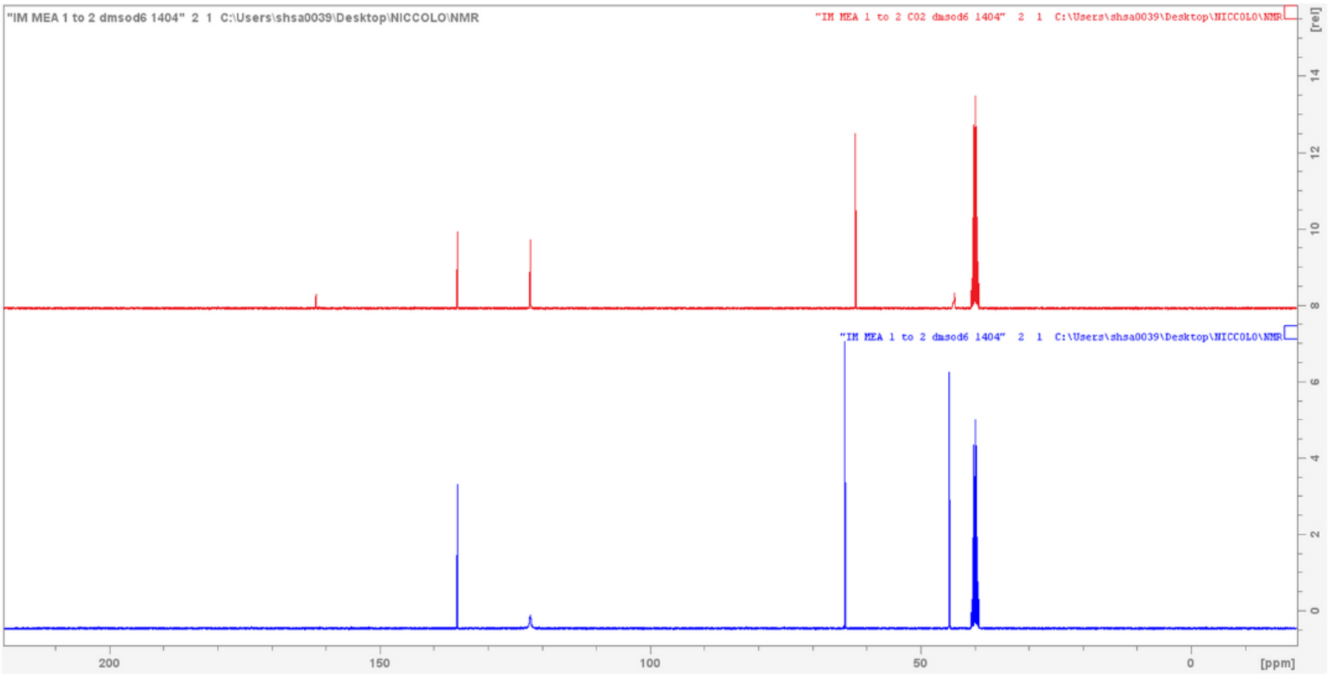


Figure 3.13: C-NMR spectre for Im-MEA (1:2)

The Nuclear Magnetic Resonance (NMR) spectroscopic analysis was employed to further characterize the DES composed of Imidazole and Diethylamine, a combination that demonstrated superior CO_2 capture capabilities. To obtain a comprehensive understanding of the solvent's structure, both carbon-13 NMR (C-NMR) and proton NMR (H-NMR) spectroscopies were utilized. The resulting spectra from these analyses are depicted in the figures below, providing insight into the molecular interactions and the chemical environment within the DES that contribute to its high CO_2 absorption efficiency. This dual-spectroscopic approach enables a detailed examination of the solvent's molecular framework, offering a more nuanced understanding of its functional groups and the dynamics of its CO_2 uptake mechanism.

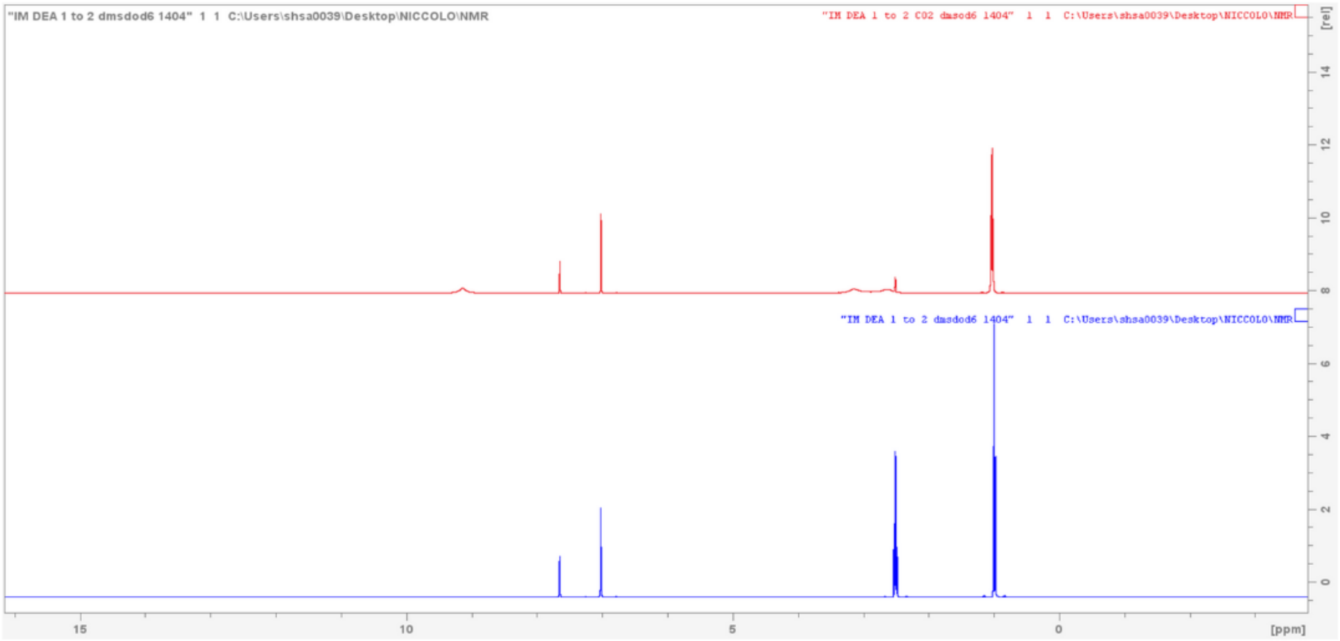


Figure 3.14: H-NMR spectre for Im-DEA (1:2)

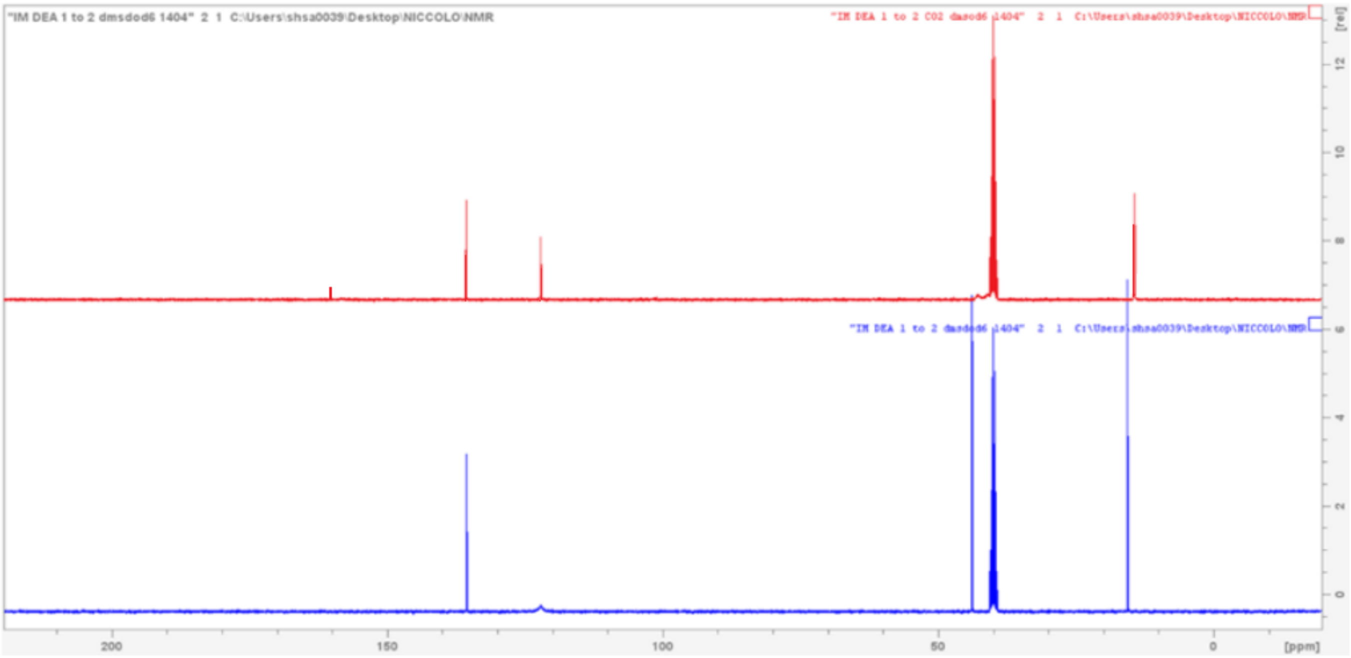


Figure 3.15: C-NMR spectre for Im-DEA (1:2)

The observations and conclusions drawn from the analysis of the initial deep eutectic solvent (DES) under investigation hold true for the subsequent DES sample as well. The carbon-13 Nuclear Magnetic Resonance (C-NMR) spectroscopic analysis corroborated the findings previously revealed by Fourier Transform Infrared Spectroscopy (FTIR). Both techniques have consistently indicated the formation of carbamate species (Peak around 160 ppm) — molecules that emerge from the chemical reaction between the solvent constituents and CO_2.

This recurrent detection of carbamate formation is a definitive sign, confirming that the DES is undergoing a reaction with CO_2 to form conjugated complexes. Such complexes are indicative of the solvent's pronounced ability to absorb CO_2. This absorption is not a mere surface interaction but a deeper chemical integration, highlighting the remarkable efficacy of this solvent in capturing and retaining CO_2.

The consistency of these findings across different analytical methods not only strengthens the reliability of the results but also enriches our understanding of the solvent's chemical behaviour. It provides unequivocal evidence of the DES's capacity for CO_2 absorption, which can be attributed to the intrinsic properties of the solvent molecules that facilitate the formation of stable carbamate complexes. This data is instrumental for confirming the solvent's potential for practical applications in CO_2 capture technologies, where high absorption capacity is a critical factor.

Studying the H-NMR spectrum of the DES in question we can notice the presence of a new peak around the value of 9 ppm.

The presence of a peak at 9 ppm in an H-NMR spectrum of a deep eutectic solvent (DES) formed from imidazole and diethylamine in a 1:2 molar ratio could be associated with protons in a carbamate (carbamate) molecule formed after CO_2 absorption.

When carbon dioxide (CO_2) is absorbed into a solution containing amines such as diethylamine, it can react with the amine to form carbamate species (carbamate). These carbamate species contain nitrogen and carbon atoms, which can cause proton resonances in the 9-ppm region in an H-NMR spectrum. The specific chemical shift can vary depending on the exact structure of the carbamate species and the local chemical environment of the protons.

The formation of carbamate, and thus the validation of the accurate interpretation of the H-NMR spectrum, is confirmed by the C-NMR results. The presence of a peak at around 160 ppm in the C-NMR spectrum confirms the previous analysis.

Further confirmation of this discovery emerges from the analysis of the FTIR spectrum, in which the peaks formed after the absorption of CO_2 leave little doubt on the formation of the carbamate.

Furthermore, comparing the data with known reference spectra of carbamates or conducting additional experiments helps to confirm this interpretation.

In reference to the study of the latest deep eutectic solvent (DES) currently under investigation, specifically that resulting from the combination of imidazole and pentaethylenehexamine (PEHA) in a molar ratio of 1:2, The investigation conducted using the preceding characterization method has revealed that the particular Deep Eutectic Solvent (DES) under examination does not exhibit significant promise in the realm of CO_2 absorption. Consequently, additional analyses and examinations have failed to yield valuable insights or contributions within this context. The findings suggest that the studied DES may not be an optimal candidate for applications related to CO_2 absorption, prompting the need for alternative solvent exploration or modifications to enhance its performance in this specific area. This outcome underscores the importance of refining our understanding of solvent behaviours and properties to align with the targeted application, thus facilitating more informed and purposeful advancements in the field of carbon capture and absorption technologies.

3.3 Electroreduction Results

3.3.1 Choice of DES

In delving into the second phase of our project, specifically focused on the electroreduction of CO_2 into refined and valuable end products, particularly CO, it is imperative to commence with a comprehensive elucidation of the DES chosen to drive the conversion process.

As previously discussed, electroreduction involves the strategic utilization of electrical energy to drive the reduction of CO_2, thereby yielding valuable end products. In this electrochemical landscape, the DES acts as a crucial component, functioning as an electrolyte medium to provide a conducive milieu for the reduction of CO_2.

In essence, the incorporation of DES as the electrolyte medium in this electroreduction study represents a deliberate and informed choice, one that aligns with the overarching objective of efficiently transforming CO_2 into valuable products.

Having examined a spectrum of Deep Eutectic Solvent options in the preceding section of this chapter, four distinct candidates have emerged as particularly noteworthy final mediums for the current undertaking. These include DES formulations comprised of Imidazole (Im) and Monoethanolamine (MEA) at varying molar ratios, specifically 1:2, 1:3, and 1:4, along with the DES amalgamation of Imidazole and Diethylamine (DEA) at a molar ratio of 1:2. Remarkably, the latter exhibited the highest CO_2 absorption values, distinguishing it as a frontrunner among the investigated DES configurations.

The decision to propel this project forward hinged upon the identification of the DES variant that demonstrated one of the most noteworthy CO_2 absorption values, namely the formulation comprising Imidazole and Monoethanolamine with a molar composition of 1:2. This particular DES exhibited a compelling efficacy in absorbing CO_2. The rationale behind this strategic selection lies in the pursuit of optimal performance and efficiency in the subsequent phases of the project, where the chosen DES will play a pivotal role in facilitating the electroreduction of CO_2 into valuable end products.

By prioritizing the DES with a molar composition of 1:2 Imidazole and Monoethanolamine, the project aims to capitalize on the promising CO_2 absorption characteristics observed during the preliminary stages. This calculated choice aligns with the overarching goal of optimizing the DES as a key catalyst and electrolyte medium for the electroreduction process, ensuring that the subsequent phases of the project are conducted with a highly effective and tailored solvent system. In essence, the careful consideration and selection of this specific DES underscore the importance of aligning the chosen medium with the project's objectives, setting the stage for a more focused and successful exploration of CO_2 electroreduction.

The preference for monoethanolamine (MEA) over diethanolamine (DEA) in certain applications, such as in the formation of Deep Eutectic Solvents (DES) for CO_2 absorption, can be attributed to several factors:

1. *Chemical Structure and Reactivity:*
   MEA has a simpler chemical structure compared to DEA. The presence of two hydroxyl groups in MEA makes it more reactive and potentially more efficient in certain chemical processes, including CO_2 absorption.
   The reactivity of MEA arises from its ability to readily form chemical bonds with CO_2 molecules, facilitating the absorption process.

2. *Solubility and Viscosity:*
   MEA may exhibit better solubility in certain solvents, contributing to the formation of a more homogeneous DES.
   The lower molecular weight of MEA result in lower viscosity compared to DEA, which could enhance the fluidity and ease of handling in specific applications.

3. *Economic Considerations:*
   MEA is often more cost-effective compared to DEA, which could influence the choice of solvent in large-scale industrial applications.

4. *Selectivity:*
   MEA exhibit higher selectivity for CO_2 absorption under certain conditions, making it a more suitable choice for applications where the specific capture of CO_2 is crucial.

5. *Environmental Impact:*
   MEA is generally considered less environmentally harmful compared to DEA, which may influence decisions in applications where environmental considerations are paramount.

The choice of 1:2 molar ratio for the deep eutectic solvent (DES) consisting of imidazole (Im) and monoethanolamine (MEA) in the electroreduction of CO_2 to CO is based on a combination of molecular, thermodynamic, and kinetic considerations. Some potential reasons why the 1:2 molar ratio might be considered best for this specific application are listed in the lines below:

1. *Eutectic point and melting point:*
   The 1:2 molar ratio corresponds to the eutectic point, where DES has the lowest melting point. A lower melting point is advantageous for maintaining DES in a liquid state, improving its functionality as an electrolyte in the electroreduction process.

2. *Optimal molecular interactions:*

The 1:2 ratio can promote favourable molecular interactions between imidazole and monoethanolamine. Strong hydrogen bonds and other interactions could improve the overall reactivity of DES with CO_2 during electroreduction.

3. *Balanced composition for CO_2 activation:*
   The balanced composition of imidazole and monoethanolamine in the ratio 1:2 provides an optimal environment for the activation of CO_2. This balance facilitates the electrochemical reduction of CO_2 to CO with improved efficiency.

4. *Electrochemical stability:*
   The 1:2 molar ratio can offer greater electrochemical stability, ensuring that the DES remains stable under the conditions of the electroreduction process. This stability is critical for long-lasting and reliable performance.

5. *Previous experimental success:*
   Previous studies have shown how this molar ratio results in very high conversions of CO_2.

Having examined the reasons behind the choice of this solvent as an electrolytic medium, attention now shifts to the operational phase of the electro-reduction process. This step marks one of the milestones of this study, where the electro-chemical mechanisms involved in the efficient transformation of carbon dioxide (CO_2) into valuable end products, are analysed in detail, using the aforementioned solvent as the key element of the system.

The theoretical underpinnings of the entire electroreduction concept were expounded upon in Chapter One during the introductory phase of the study. In this subsequent section, our focus shifts towards a comprehensive examination of the outcomes stemming from the electroreduction of CO_2.

The electrolyte cells employed in this conversion experiment, along with their operational parameters, have been elucidated in prior discussions.

3.3.2 Characterization of N-CND for the Electroreduction

Within the electro-reduction segment of our research, the selection of a specific electrode holds paramount significance, as it serves as a pivotal factor in achieving a more precise and efficient conversion of CO_2 into the desired end product. Delving into the intricacies of this study, as extensively discussed, and elucidated in preceding chapters, a distinctive electrode derived from Spruce Needles has been chosen as the working electrode due to its demonstrated high success rates in this particular realm.

Prior to the actual implementation of the conversion process, a synthesis of 6 N-CNDs (Nitrogen-Doped Carbon Nanodots) was undertaken. These synthesized materials underwent a series of comprehensive characterization tests, including Raman spectroscopy, BET (Brunauer–Emmett–Teller) surface area analysis, and TPD (Temperature-Programmed Desorption). The purpose of these assessments was to discern and ascertain the most suitable N-CND variant that would subsequently be employed in the fabrication of the working electrode.

The synthesized 6 N-CNDs are detailed below, each representing a distinct approach in their production and modification processes:

1. **Spruce Needles with Electrochemical Conversion (EC):**
   This variant involves the electrochemical conversion of Spruce Needles to generate N-CNDs, showcasing the potential for electrochemically induced transformations in the synthesis process.

2. **Spruce Needles with Chemical Modification (CM):**
   In this approach, Spruce Needles undergo chemical modification to yield N-CNDs, highlighting the versatility of chemical processes in tailoring the properties of the carbon nanodots.

3. **Fraction 3 with Electrochemical Conversion (EC):**
   N-CNDs are produced through electrochemical conversion specifically from Fraction 3, elucidating the role of particular fractions in the raw material as a source for controlled synthesis.

4. **Fraction 3 with Chemical Modification (CM):**
   This method involves the chemical modification of N-CNDs derived from Fraction 3, underscoring the adaptability of chemical processes in the modification phase of the synthesis.

5. **Twigs with Electrochemical Conversion (EC):**
   N-CNDs are synthesized through electrochemical conversion using twigs as the primary material, showcasing the potential of different plant components in the electrochemical route.

6. **Twigs with Chemical Conversion (CM):**
   This approach involves the chemical conversion of twigs to produce N-CNDs, emphasizing the applicability of chemical methods in creating carbon nanodots from alternative botanical sources.

Each method in this comprehensive list not only broadens the spectrum of N-CND synthesis but also provides valuable insights into the varied avenues of electrochemical and chemical approaches, paving the way for a nuanced understanding of the intricacies involved in tailoring carbon nanodots for specific applications.

3.3.2.1 Raman Analysis

The graphic below depicts the Raman spectroscopy spectrum obtained through a comprehensive analysis conducted on all synthesized samples. This spectroscopic examination serves as a critical tool in characterizing the structural and vibrational properties of the materials under investigation. This in-depth spectral analysis serves as a foundation for drawing correlations between the experimental parameters and the resulting material characteristics, contributing to a more comprehensive and nuanced comprehension of the synthesized samples' properties.

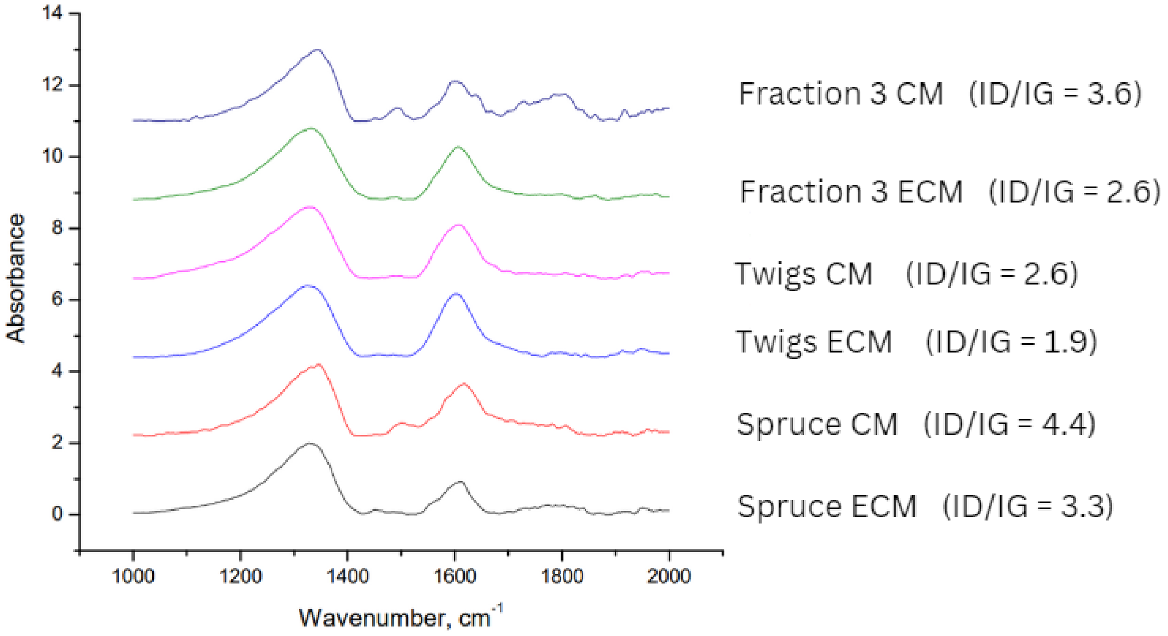


Figure 3.16: Raman spectre for different N-CNDs

Observing the results, it becomes apparent that the N-CND synthesized from chemically modified spruce needles exhibits a notably higher ID/IG factor compared to the other variants. The elucidation for this observed phenomenon is provided in the subsequent lines.

The ID/IG ratio in Raman spectroscopy is a significant parameter because it provides valuable information about the structural and compositional characteristics of carbon materials, particularly those with a graphene-like structure. In Raman spectroscopy, the ID (disorder-induced) and IG (graphitic) peaks correspond to specific vibrational modes associated with the sp_3-hybridized carbon atoms (ID) and the sp_2-hybridized carbon atoms in graphitic structures (IG).

The choice of N-NCDs (nitrogen-doped carbon nanodotes) with a higher ID/IG ratio is based on the following points:

1. *Custom Material Properties:*

The ID/IG ratio is indicative of the degree of disorder and structural defects in carbon materials. Choosing an N-NCD with a higher ID/IG ratio is important to tailor specific material properties, such as increased surface reactivity or modified electronic properties.

2. *Improved catalytic activity:*

Higher levels of disorder create more active sites on the surface of carbon materials.

N-NCDs with a higher ID/IG ratio exhibit enhanced catalytic activity, making them desirable for applications in catalysis and electrocatalysis.

3. *Sensitivity to functionalization*

The ID/IG ratio is sensitive to chemical functionalization or changes in carbon structure.

The choice of N-NCD with an ID/IG ratio is optable when you want to perform subsequent functionalizations and when you want a material that responds to these changes.

4. *Understanding the Effects of Nitrogen Doping:*

Nitrogen doping is known to introduce structural changes in carbon materials.

A higher ID/IG ratio in N-NCDs is preferable to study the influence of nitrogen doping on the overall disorder and electronic structure of the nanodots.

5. *Controlled Defect Engineering:*

Controlled introduction of defects is a strategy in materials engineering for specific applications.

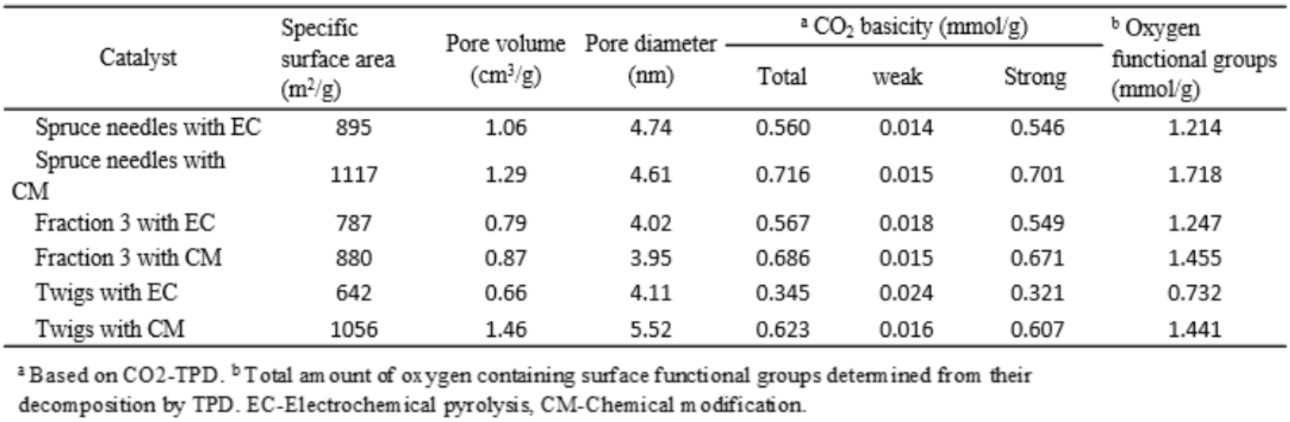
N-NCDs with higher ID/IG ratio are intentionally synthesized to introduce controlled defects for targeted applications, such as sensing or energy storage.

Based on the Raman spectrum, the optimal choice for proceeding with the subsequent electro-reduction is the N-CND synthesized from chemically modified spruce needles.

3.3.2.2 BET and TPD Characterisation

The outcomes stemming from the BET and TPD characterizations have been documented and are presented in the tabulated format below. This table encapsulates the key findings from the analyses, providing a comprehensive overview of the surface area characteristics and the thermal desorption properties of the synthesized materials. The data extracted from the BET analysis sheds light on the specific surface area, porosity, and adsorption properties, while the TPD results offer insights into the thermal stability and desorption behaviour of the synthesized samples.

Table 3.3: BET and TPD results for differents N-CNDs



Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	[a] CO_2 basicity (mmol/g)			[b] Oxygen functional groups (mmol/g)
				Total	weak	Strong	
Spruce needles with EC	895	1.06	4.74	0.560	0.014	0.546	1.214
Spruce needles with CM	1117	1.29	4.61	0.716	0.015	0.701	1.718
Fraction 3 with EC	787	0.79	4.02	0.567	0.018	0.549	1.247
Fraction 3 with CM	880	0.87	3.95	0.686	0.015	0.671	1.455
Twigs with EC	642	0.66	4.11	0.345	0.024	0.321	0.732
Twigs with CM	1056	1.46	5.52	0.623	0.016	0.607	1.441

[a] Based on CO2-TPD. [b] Total amount of oxygen containing surface functional groups determined from their decomposition by TPD. EC-Electrochemical pyrolysis, CM-Chemical modification.

The concentration of basic sites and the overall amount of surface oxygen-containing groups in the carbon samples were evaluated using temperature-programmed desorption (TPD) on a BELCAT II instrument. The CO2-TPD profiles of N-doped carbons revealed distinct desorption peaks around 110–120 °C and 240–340 °C. These observed peaks align closely with results reported in the literature and are indicative of the existence of Lewis basic sites on the surface of N-CNDs, which incorporate pyridinic, pyridonic, and quaternary nitrogen species. The consistency between our results and established data strengthens the understanding of the surface chemistry of N-doped carbons, particularly highlighting the presence of specific nitrogen functionalities associated with basic sites.
Identifying distinct temperature peaks in the 200 to 360°C range in CO_2-TPD profiles adds a layer of specificity to characterization efforts. In particular, the low temperature peak observed below 200 °C was attributed to the presence of carboxyl groups on the carbon surface. This identification is critical to understanding the chemicalcomposition, as carboxyl groups are known for their distinctive reactivity and potential influence on surface interactions.

In contrast, high temperature peaks observed above the 300–360 °C range were associated with lactones and phenolic groups. This distinction is significant since lactone and phenolic functionalities contribute to the overall heterogeneity of surface oxygen-containing groups.

This information not only contributes to a better understanding of surface chemistry, but also provides a basis for tailoring the material for specific applications by strategically manipulating the abundance and distribution of these oxygen-containing groups.

In the present investigation, carbon samples derived from pyrolysis at 350 °C exhibited predominantly mesoporous and microporous characteristics, as evidenced by a substantial BET specific surface area ranging from 642 to 1117 m2/g. This noteworthy porosity highlights the potential for improved adsorption and catalytic activities of the material under investigation.

Motivated by these distinctive properties, the focus of the present study is aimed at the development of a Co-DAC (cobalt-doped activated carbon) catalyst supported on a porous, acidic and robust CND (Carbon Nanodot) solid matrix sourced from spruce needles. Using a porous matrix derived from spruce needles not only takes advantage of the natural abundance of this renewable resource, but also takes advantage of the structural and chemical attributes of the resulting carbon nanodots.

The incorporation of cobalt into the activated carbon matrix increases the potential for catalytic applications, particularly due to the synergistic effects between the catalytic properties of the cobalt species and the porous nature of the carbon matrix. This strategic approach aims to exploit the intrinsic acidity and structural stability of the solid CND matrix, optimizing catalyst performance for targeted applications.

In essence, the use of mesoporous and microporous carbon samples, combined with the integration of cobalt-doped activated carbon supported on a robust CND matrix, constitutes a deliberate effort to design and engineer materials with properties tailored for catalytic and adsorption.

Then, based on information from Raman spectroscopy, comprehensive characterization tests further affirm that the prominent N-CND variant emerges from chemically modified spruce needles.

Notably, surface area analysis reveals that N-CND synthesized from chemically modified spruce needles boasts a specific surface area of 1117 m2/g. This remarkable surface area is a key factor as it indicates greater reactivity, adsorption capacity and potential applications in different fields.

Furthermore, the quantification of strong basic sites, with a notable value of 0.701, further accentuates the superiority of N-CND derived from chemically modified spruce needles. The presence of strong basic sites is critical in influencing the catalytic activity and reactivity of the material, making it a promising candidate for applications where higher basicity is a desirable characteristic.

In essence, the synthesis of N-CNDs from chemically modified spruce needles emerges not only as a spectroscopically favourable but also strategically advantageous choice, as stated by the high surface area and abundance of strong basic sites.

After the selection of the optimal N-CND, the start of the electroconversion process is initiated. The procedural actions for this electroconversion have been comprehensively outlined in the second chapter, in particular within the section dedicated to the experimental set-up for the conversion phase.

3.3.2.3 EDX Analysis

While studying the chosen N-CND for use in carbon dioxide (CO_2) electroreduction, a comprehensive analysis was also conducted using energy dispersive X-ray spectroscopy (EDX). This analytical technique facilitated an in-depth exploration of the internal structure of N-CND, allowing the identification and characterization of the specific components that constitute the final material.
The resulting analysis is depicted in the images presented here.

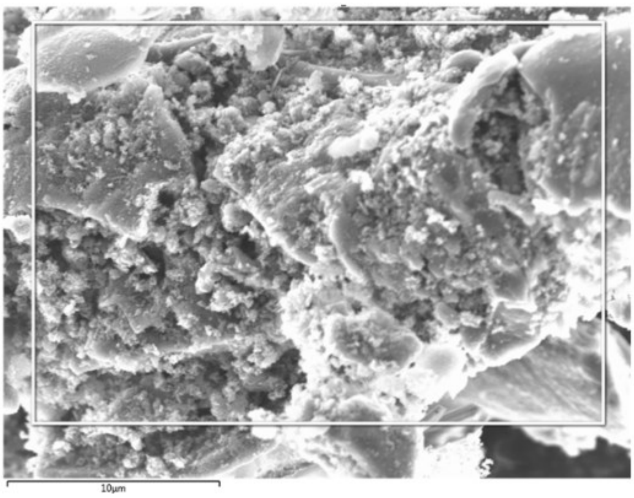


Figure 3.17: EDX of N-CND from CM Spruce Needles

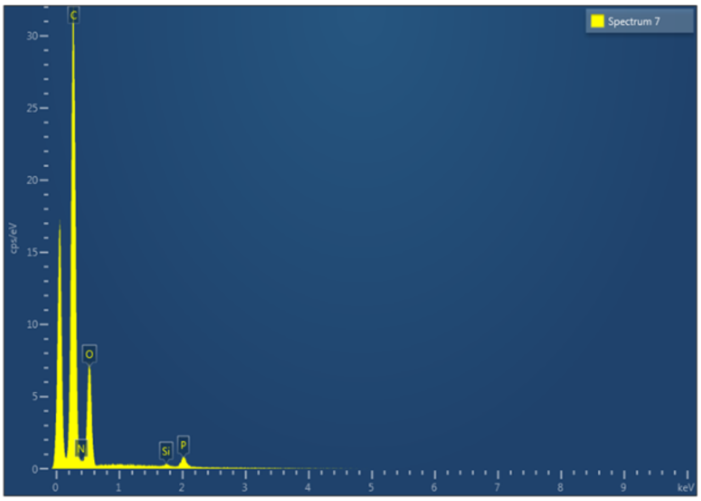


Figure 3.18: Atomic distribution of N-CND from CM Spruce Needles

In the table below, the various components and their respective percentages are reported:

Table 3.4: Atomic distribution in percetage of N-CND from CM Spruce Needles

Element	Line Type	Apparent Concentration	K Ratio	Wt%
C	K series	164.53	1.64529	71.41
N	K series	1.16	0.00804	0.67
O	K series	41.67	0.36509	21.36
Si	K series	1.98	0.01814	0.8
P	K series	11.51	0.12475	5.76
Total				100

3.3.2.4 GC-SM Analysis

As previously clarified in chapter two within the experimental setup section, CO_2 reduction was performed at a potential of -1.2 V (relative to Ag/AgCl) and the resulting CO products were monitored for a duration of 3600 seconds. The rationale behind choosing a potential of -1.2 V and duration of 3600 seconds lies in their importance in capturing the dynamics and efficiency of CO_2 reduction under controlled experimental conditions.

As part of the analysis of gaseous products, the examination was conducted using gas chromatography-mass spectrometry (GC-MS). This analytical technique facilitated the investigation of the composition of gaseous products, offering detailed insights into their molecular structures and identifying the various compounds present. The use of GC-MS not only enabled the separation of individual components in the gas mixture, but also provided precise mass spectrometric data for accurate identification.

The spectral data of the analysis conducted are shown in the following images.

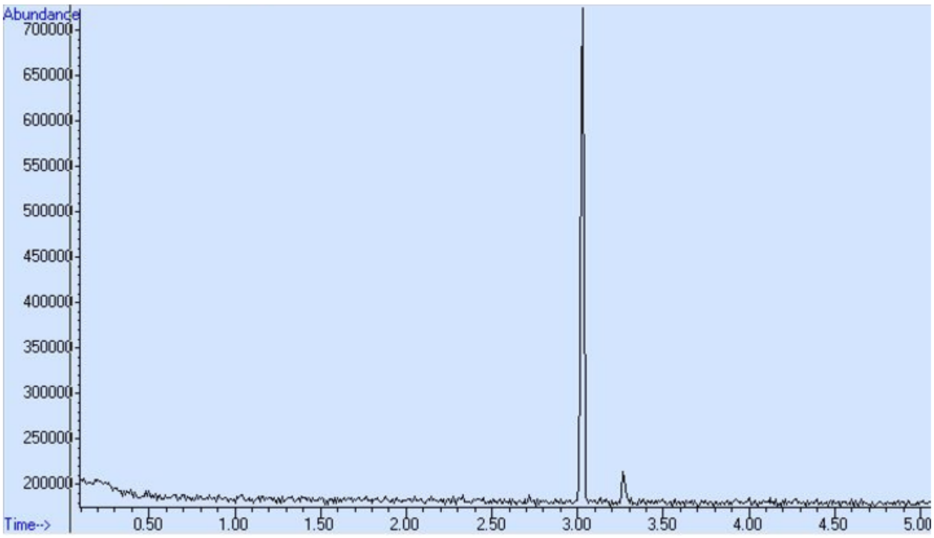


Figure 3.19: GC-MS Spectre for the gas phase after the electroreduction

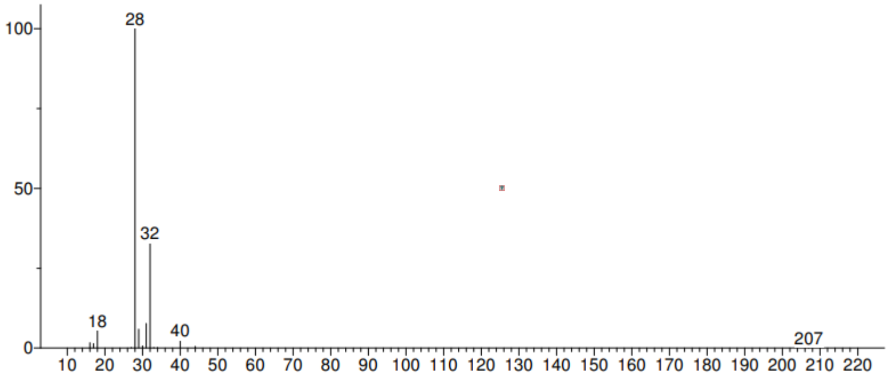


Figure 3.20: peak analysis within the GC-MS spectrum

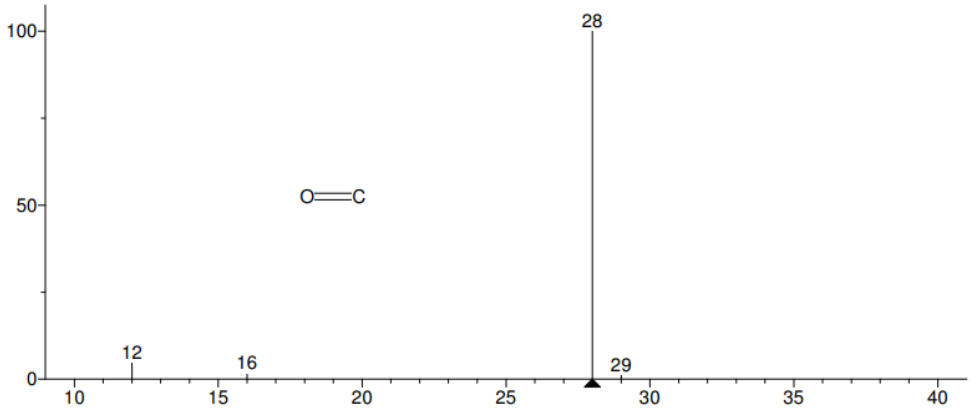


Figure 2.21: CO identification into the GC-MS spectrum

The initial trio graph visually portrays the levels of gas abundance present in the analysed sample. Within this comprehensive analysis, a distinct compound emerges, showing an abundance above 700,000 on the gas chromatography-mass spectrometry (GC-MS) scale. This conspicuous dominance underlines the importance of this particular compound, suggesting its prevalence and potential importance in the composition of the gas under consideration.

The quantification and presentation of abundance levels provide a clear perspective on the hierarchical distribution of compounds within the sample.

In subsequent graphical representations, close observation reveals the alignment of the specific composition of the gas with a distinct region on the x-axis, denoted by the value 28. This particular axis represents the mass-to-charge ratio (m/z) in the context of gas chromatography-mass spectrometry. In particular, an m/z value of 28, according to mass spectroscopy conventions, is indicative of carbon monoxide (CO).

This correlation within the mass spectrum provides crucial insight into the chemical identity of the predominant gas species present in the analysed sample. The association with carbon monoxide constitutes convincing confirmation that the electroreduction process occurred as expected. The initial absorption of CO_2 within the deep eutectic solvent (DES) successfully underwent transformation, resulting in the production of carbon monoxide.

This alignment between the expected result and the observed gas composition confirms the effectiveness of the electroreduction mechanism, as evidenced by the targeted conversion of the absorbed CO_2 into the expected chemical.

3.3.2.5 NMR Analysis

A comprehensive investigation into the liquid-phase products was undertaken through the application of 13C NMR analyses. The experiments were conducted utilizing a Bruker Avance 400 MHz spectrometer, which enabled precise and high-resolution spectroscopic measurements.
The spectra corresponding to three distinct phases of the experimental process are illustrated below, offering a complete view of the dynamic evolution of the system.

- *Pure DES analysis (without CO_2):*
  The first spectrum clarifies the molecular characteristics of the deep eutectic solvent (DES) in its original state, devoid of any influence of CO_2. This initial analysis serves as a basic reference, providing essential information on the intrinsic properties of the solvent before undergoing chemical transformations.

- *Analysis after CO_2 absorption:*
  Following the absorption of carbon dioxide (CO_2), the second spectrum captures the altered chemical composition of the system. This analysis is instrumental to identify and quantify the changes induced by the interaction between DES and CO_2.

- *Analysis after conversion by electrolytic cell:*
  The third spectrum portrays the molecular situation that follows the electroreduction process inside the electrolytic cell. This step represents a crucial transformation, in which the CO_2 initially absorbed in the DES undergoes conversion. By comparing this spectrum with the previous ones, it becomes possible to discern the specific alterations of the molecular structure.

Collectively, these three spectra serve as complex snapshots, allowing a step-by-step exploration of the molecular changes occurring during the experimental sequence, contributing to an improved understanding of the dynamic interaction between the deep eutectic solvent, carbon dioxide, and electrochemical conversion process.

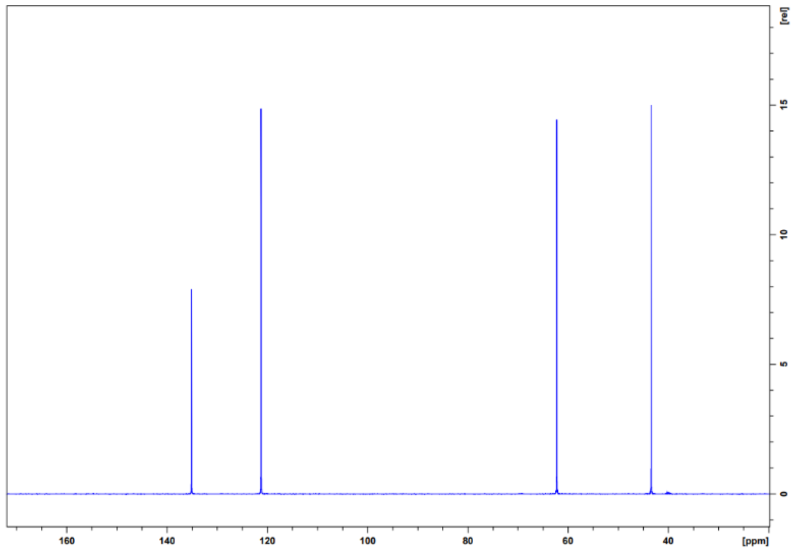


Figure 3.21: C-NMR spectre for Pure DES

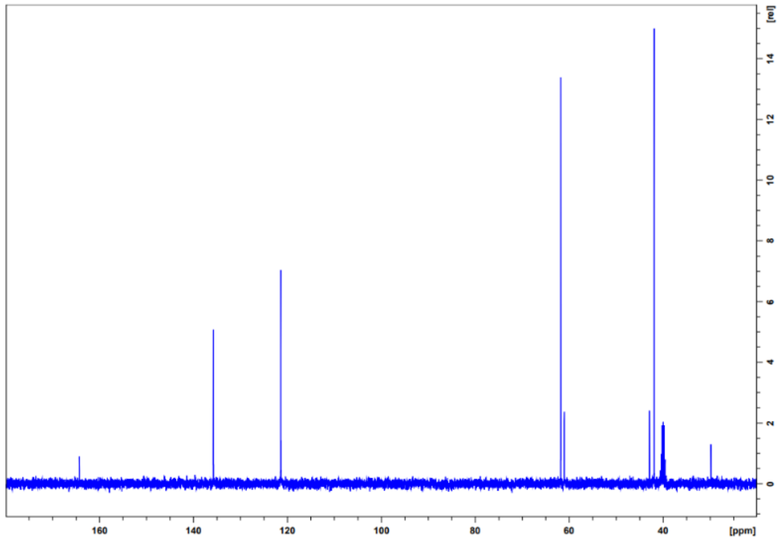


Figure 3.22: C-NMR spectre for DES after CO_2 absorption

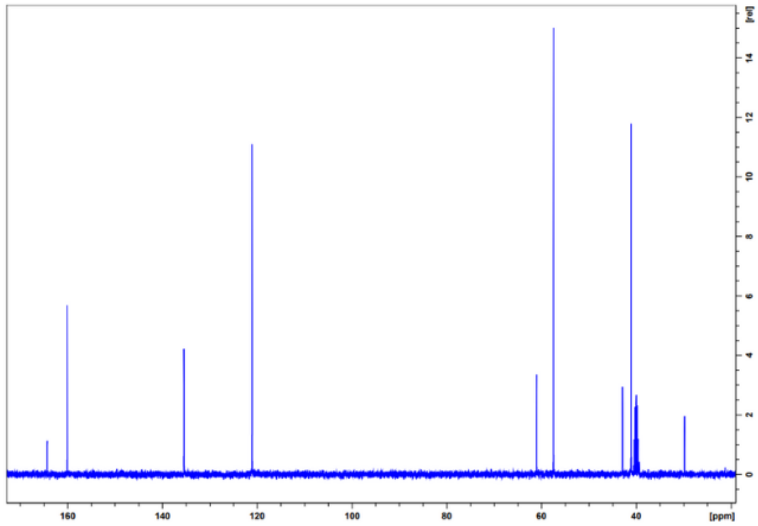


Figure 3.23: C-NMR spectre for the DES after the CO_2 conversion

Within the spectrum of the second analysis, particularly that of the deep eutectic solvent (DES) containing absorbed CO_2, a distinctive peak associated with the carbamate ion becomes evident. The theoretical bases of this phenomenon have been thoroughly explored and explained in the dedicated section.

Moving on to the spectrum derived from the third analysis, which corresponds to the DES following electroreduction, a convincing revelation emerges. In addition to the characteristic peak of the carbamate ion, there is another prominent peak of substantial importance, located at approximately 160 ppm. The appearance of this additional peak suggests the presence of a molecular entity or structural portion that is closely linked to the electroreduction process.

CONCLUSIONS

The purpose of this thesis was to evaluate and study a number of Deep Eutectic Solvent (DES) to absorb carbon dioxide and subsequently convert it into valuable end products. Deep eutectic solvents (DES) are a type of ionic liquid that has gained attention as an environmentally friendly and sustainable alternative to traditional solvents. Unlike conventional solvents, which are often derived from petrochemicals and may pose environmental and health risks, deep eutectic solvents are typically composed of simple and biodegradable components. The term "eutectic" refers to a mixture with a lower melting point than that of its individual components. In the case of deep eutectic solvents, these mixtures often involve a combination of a hydrogen bond donor (such as a quaternary ammonium salt or a metal halide) and a hydrogen bond acceptor (usually a metal chloride or a metal oxide). Throughout this investigation, we proved that DES could provide a significant advantage in carbon dioxide absorption compared to conventional absorption solutions. The main advantages of these solvents compared to traditionally used solvents lie in their broader liquid range and high thermal stability. Many DES are formed from low-cost and environmentally benign chemical species. The study focused on five DES (Im-MEA (1:2), Im-MEA (1-3), Im-MEA (1-4), Im-DEA (1-2), Im-PEHA (1-2)) suitable for chemical absorption and two (TPAB-Formic Acid (1:2), TPAB-Acetic Acid (1:2)) for physical absorption.

A comparison of the CO_2 absorption between one of the studied solvents, Im-DEA (1:2), and a well-researched CO_2 absorption solvent, choline chloride/urea (1:2), provides an estimate of the advantages of using these solvents. Maximum absorption values for the latter solvent are around 0.18/0.19 Kg_{CO2}/Kg_{DES}, as reported in studies by Yujiao Xie at Lulea University in her licentiate thesis 'CO_2 Separation with Ionic Liquids -Property, Gas Solubility and Energy Consumption' and Xiaoyan Ji et al. in their article 'CO_2 capture/separation using choline chloride-based ionic liquids' [31, 32]. In contrast, the maximum absorption value for Im-DEA (1:2) is approximately 0.31 kg_{CO2}/kg_{DES}.

It was observed that temperature negatively affects the effectiveness of these solvents, suggesting that working at lower temperatures is preferable. To compare absorption values at different temperatures, we can reference the absorption tests conducted on the DES Im-MEA (1:2) at temperatures of 25 and 45 degrees Celsius. At the initial temperature, an absorption value of 2.41 mol_{CO2}/Kg_{DES} was observed, while at the higher temperature, the value decreased significantly to 1.81 mol_{CO2}/Kg_{DES}. This indicates a substantial reduction in absorption as the temperature increases. The reasons behind this phenomenon are primarily that an increase in temperature promotes the desorption of CO_2, shifting the reaction equilibrium in that direction. Additionally, the solvent's viscosity decreases, resulting in fewer interactions between the solvent and carbon dioxide.

This aspect can be advantageous in terms of plant costs since there is no need to heat the solvent to activate its absorption properties.

Furthermore, the study investigated the behaviour of various deep eutectic solvents (DES) with identical components but differing in molar ratios (Im-MEA (1:2), Im-MEA (1:3), Im-MEA (1:4)). It was observed that as the amine concentration within the solvent increased, the amount of absorbed CO2 also increases. Monoethanolamine, characterized as a primary amine, features a primary amino group (NH2) that exhibits greater reactivity with CO_2 compared to secondary or tertiary amines. This heightened reactivity stems from the presence of a free hydrogen atom on the nitrogen in primary amines, facilitating the formation of a chemical bond with CO_2.

In a deep eutectic solvent, the amine groups in monoethanolamine (MEA) serve as sites for CO_2 absorption. By elevating the molar ratio of MEA in the DES, more primary amine groups are introduced into the solution. Consequently, an increased number of active sites become available for CO_2 molecules to bind to, thereby enhancing the overall capacity of the solvent to absorb CO_2.

The study also investigated the absorption values between chemical absorption DES and those for physical absorption. It was observed that DES for chemical absorption exhibited higher absorption capacity. To provide a numerical comparison, the absorption values for Im-DEA (1:2) and TPAB-Formic Acid (1:2) are reported: 0.30 Kg_{CO2}/Kg_{DES} for Im-DEA (1:2) and 0.07 Kg_{CO2}/Kg_{DES} for TPAB-Formic Acid (1:2). The discrepancy in this value is attributable to the fact that physical absorption involves weaker intermolecular bonds and to the greater selectivity for CO2 in DES employed for chemical absorption.

To visually confirm the interaction between CO2 and the solvent, FTIR and NMR analyses were conducted, clearly revealing the formation of carbamate ions. In this context, a study of the chemical properties was also undertaken by combining the group functional method with the Combing and Mixture rules. Critical properties were calculated, including critical density, which exhibited the remarkable characteristic of not deviating significantly from the density calculated at ambient temperature. This value can thus, with a degree of uncertainty, be employed to estimate the density at ambient temperature in cases of unknown values.

The second crucial step involves the electrolytic conversion of CO_2 using DES as an electrolytic medium and N-CND as a working electrode to enhance the conversion process. Producing and electrode directly from biomass, specifically spruce needles, has been recognized as a promising method to improve the electrocatalytic reduction of CO_2. N-doped porous carbon materials were produced for our study using a one-step process, activating nitrogen-enriched biomass from Spruce needles. In summary, biomass particles were combined with a 50% aqueous phosphoric acid solution, left to sit for 24 hours, transferred to ceramic crucibles, and heated to 500 degrees Celsius for 1 hour. The resulting doped carbon materials were transformed into powder, washed in hot deionized water, dried at 100 degrees Celsius for 24 hours, and preserved for future use. In the electrode preparation, 10 mg of N-doped Carbon Nano Dots (N-CND) was mixed with a solution of 30 μL Nafion 117 and 970 μL ethanol. After 30 minutes of blending and sonication, a 50-μL portion of the slurry was coated onto a 0.5 by 2.0 cm Toray Carbon Paper (TGP-H-090) and air-dried for solvent evaporation, solidifying the electrode material.

This biomass-derived electrode serves as a catalyst for the reduction process, and its effectiveness can be further amplified by utilizing a substrate made of cobalt-doped carbon paper. Moreover, using an electrode entirely derived from renamable sources contributes to sustainable practices.

In this study, the set objective has been achieved: the conversion of CO2 into a valuable product, specifically CO, which is currently employed in various industrial processes. While the quantity produced has not been calculated, it will undoubtedly be the next focus in the continuation of this research.

In summary, this study aimed to identify a method for capturing and converting carbon dioxide into a valuable component using solvents and electrodes derived from non-polluting products.

APPENDIX

Table 1: Absorption values for Im-MEA (1:2).

P [MPa]	X_{CO2} [mol/mol]	M_{CO2} [mol/kg]
0.478466	0.15593907	2.4524
0.427759	0.188676352	2.9672
0.600983	0.192090159	3.0209
0.779537	0.196267383	3.0866
0.969147	0.199597002	3.1390
1.14183	0.203594815	3.2018
1.28603	0.206937277	3.2544
1.43942	0.209316965	3.2918
1.60343	0.211473506	3.3257
1.74336	0.214287886	3.3700
1.88774	0.216348278	3.4024

Table 2: Absorption values for Im-DEA (1:2)

P [MPa]	X_{CO2} [mol/mol]	M_{CO2} [mol/kg]
0.4773	0.2684	3.7534
0.4189	0.3498	4.8914
0.5143	0.3782	5.2873
0.7167	0.4050	5.6629
0.8844	0.4252	5.9448
1.0551	0.4424	6.1858
1.1969	0.4518	6.3165
1.3542	0.4654	6.5074
1.4926	0.4770	6.6697
1.6525	0.4906	6.8595
1.7870	0.5011	7.0057

Table 3: Absorption values for Im-PEHA (1:2)

P [MPa]	X_{CO2} [mol/mol]	M_{CO2} [mol/kg]
0.4745	0.0199	0.0945
0.6131	0.0378	0.1796
0.8093	0.0567	0.2694
0.9961	0.0739	0.3508
1.1586	0.0903	0.4286
1.2974	0.1064	0.5053
1.4773	0.1222	0.5802
1.6238	0.1388	0.6588
1.7698	0.1488	0.7064

Table 4: Absorption values for Im-MEA (1:2)

Pressure	**X_$_{CO_2}$**	**M_$_{CO_2}$**
0.4063	0.1055	1.6638
0.4752	0.1118	1.7621
0.6989	0.1179	1.8585
0.8677	0.1238	1.9513
1.0398	0.1287	2.0287
1.2198	0.1332	2.1006
1.3594	0.1366	2.1532
1.5082	0.1420	2.2393
1.6768	0.1482	2.3359
1.8135	0.1526	2.4066

Table 5: Absorption values for Im-MEA (1:3)

Pressure	**X_$_{CO_2}$**	**M_$_{CO_2}$**
0.4106	0.1342	2.1361
0.4682	0.1421	2.2620
0.6850	0.1487	2.3664
0.8646	0.1542	2.4536
1.0508	0.1601	2.5481
1.1919	0.1636	2.6033
1.3485	0.1691	2.6907
1.4956	0.1744	2.7765
1.6645	0.1796	2.8583
1.8116	0.1849	2.9427

Table 6: Absorption values for Im-MEA (1:4)

Pressure	**X_$_{CO_2}$**	**M_$_{CO_2}$**
0.4835	0.1599	2.5589
0.5395	0.1663	2.6622
0.7298	0.1742	2.7883
0.8975	0.1832	2.9317
1.0825	0.1909	3.0545

1.2370	0.1983	3.1735
1.3721	0.2046	3.2738
1.5408	0.2089	3.3436
1.6857	0.2146	3.4339
1.8290	0.2189	3.5040

Bibliography

1. *Elena Tommasi Et All, Deutectic solvents: liquidi ionici "green" di nuova generazione", settembre/ottobre 2017.*

2. *Jing Xue et all. Processing of Functional Composite Resins Using Deep Eutectic Solvent", October 2020.*

3. *Aroa R. Mainar et all. An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc" journal of Energy Storage 15 (2018) 304–328.*

4. *P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, Chem. Commun., 2003, 70–71.*

5. *X. Li, M. Hou, B. Han, X. Wang and L. Zou, J. Chem. Eng. Data, 2008, 53, 548–550.*

6. *M. Francisco, A. van den Bruinhorst and M. C. Kroon, Angew. Chem., Int. Ed., 2013, 52, 3074–3085.*

7. *R. B. Leron, A. Caparanga and M. Li, J. Taiwan Inst. Chem. Eng., 2013, 44, 879–885.*

8. *R. B. Leron and M. Li, Thermochim. Acta, 2013, 551, 14–19.*

9. *L. L. Sze, S. Pandey, S. Ravula, S. Pandey, H. Zhao, G. A. Baker and S. N. Baker, ACS Sustainable Chem. Eng., 2014, 2, 2117–2123.*

10. *H. Ghaedi, M. Ayoub, S. Sufian, A.M. Shariff, S.M. Hailegiorgis, S.N. Khan, CO2 capture with the help of Phosphonium-based deep eutectic solvents, J. Mol. Liq. 243 (2017) 564–571.*

11. *N. Zhang, Z. Huang, H. Zhang, J. Ma, B. Jiang, L. Zhang, Highly efficient and reversible CO2 capture by task-specific deep eutectic solvents, Ind. Eng. Chem. Res. 58 (2019) 13321–13329.*

12. *Gregorio García, Santiago Aparicio, Ruh Ullah, Mert Atilhan, Deep Eutectic Solvents: Physicochemical Properties and Gas Separation Applications, 2015 American Chemical Society.*

13. *Mohsin, T.A. Al-Attas, K.Z. Sumon, J. Bergerson, S. McCoy, M.G. Kibria, Economic and environmental assessment of integrated carbon capture and utilization, Cell Reports Phys. Sci. 1 (2020) 100104.*

14. *Chen, F. Li, Y. Zhang, C.L. Bentley, M. Horne, A.M. Bond, J. Zhang, Electrochemical reduction of carbon dioxide in a monoethanolamine capture medium, ChemSusChem 10 (2017) 4109e4118, https://doi.org/10.1002/ cssc.201701075.*

15. *M. Abdinejad, Z. Mirza, X.A. Zhang, H.B. Kraatz, Enhanced electrocatalytic activity of primary amines for CO2 reduction using copper electrodes in aqueous solution, ACS Sustain. Chem. Eng. 8 (2020) 1715e1720.*

16. *K.K. Maniam, S. Paul, Ionic liquids and deep eutectic solvents for CO2 conversion technologies—a review, Materials 14 (2021) 4519.*

17. *Biao Li et all. Thermodynamic study on carbon dioxide absorption in aqueous solutions of choline-based amino acid ionic liquids, Separation and Purification Technology 214 (2019) 128-138.*

18. *Jonathan Albo et all, ChemInform Abstract: Towards the Electrochemical Conversion of Carbon Dioxide into Methanol, February 2015, Green Chemistry.*

19. *Rebelo, L. P.; Canongia, J. N.; Esperanca, J. M.; Filipe, E. On theCritical Temperature, Normal Boiling Point, and Vapor Pressure of IonicLiquids.J. Phys. Chem. B2005,109(13), 6040-6043.*

20. *Joback, K. K.; Reid, R. Estimation of Pure Component Propertiesfrom Group Contribution.Chem. Eng. Commun.1987,57, 233-247.*

21. *Lydersen, A. L.Estimation of Critical Properties of OrganicCompounds. Report 3; University of Wisconsin, College of Engineering,Engineering Experimental Station: Madison, WI, 1955.*

22. *Alvarez, V. H.; Valderrama, J. O. A modified Lydersen-Joback-Reid method to estimate the critical properties of biomolecules. Alimentaria2004,254,55-66.*

23. *Valderrama J.O.; Robles P.A. Critical Properties, Normal Boiling Temperatures, and Acentric Factors of FiftyIonic Liquids. nd. Eng. Chem. Res.2007,46,1338-1344.*

24. *Valderrama, J. O.; Abu-Shark, B. Generalized Correlations for theCalculation of Density of Saturated Liquids and Petroleum Fractions.FluidPhase Equilib.1989,51,87-100.*

25. *Spencer, C. F.; Danner, R. P. Improved Equation for Prediction ofSaturated Liquid Density.J. Chem. Eng. Data1972,17, 236-241.*

26. *Rudkin, J. Equation predicts vapor pressures.Chem. Eng.1961, April 17, 202-203.*

27. *R.C Reid, J.M. Prausnitz, T.K. Sherwood, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, NY, 1987.*

28. *Kai Zhang, Yucui Hou, Yiming Wang, Kun Wang, Shuhang Ren, and Weize Wu. Efficient and Reversible Absorption of CO2by Functional DeepEutectic Solvents, EnergyFuels2018, 32, 7727−7733© 2018 American Chemical Society7727.*

29. B. Jiang, J. Ma, N. Yang, Z. Huang, N. Zhang, X. Tantai, Y. Sun, L. Zhang, Superbase/ acylamido-based deep eutectic solvents for multiple-site efficient CO2 absorption, Energy Fuel 33 (2019) 7569–7577.

30. Shokat Sarmad, a Yujiao Xie,a Jyri-Pekka Mikkolabc and Xiaoyan Jia, Screening of deep eutectic solvents (DESs) as green CO2 sorbents: from solubility to viscosity. New J. Chem., 2017.

31. Yujiao Xiea , Yingying Zhanga,b, Xiaohua Lub, CO2 capture/separation using choline chloride-based ionic liquids Xiaoyan Jia*, 2013

32. Yujiao Xie, CO2 Separation with Ionic Liquids -Property, Gas Solubility and Energy Consumption, December 2014.

Web sites:
https://webbook.nist.gov/chemistry/
https://pubchem.ncbi.nlm.nih.gov/

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