

# Ternary Azole-Based Deep Eutectic Solvents for Carbon Dioxide Capture

## 1. Scientific goal of the project

This project aims to **systematically characterize a group of ternary azole-based deep eutectic solvents (DESs) that contain an azolide salt (acting as an H-bond acceptor, HBA) and two other components (H-bond donors, HBDs), to achieve high carbon dioxide (CO<sub>2</sub>) uptake at ambient pressure while enabling low-temperature, low-energy regeneration.** We expect that the results will allow us to develop a modern experimental–computational platform for next-generation ternary DES systems, enabling the “tuning” of key properties such as viscosity, absorption enthalpy, and kinetic rate for effective and efficient material design, a growing need across many industrial branches.

DESs seem to be a promising solution as a potential replacement for the amine aqueous solutions in the CO<sub>2</sub> capture process, which, although commercialized, have certain disadvantages, such as high energy consumption and corrosive properties. Two mechanisms can be responsible for carbon dioxide absorption in liquid systems: physical and chemical absorption. The main disadvantage of physical absorption is its relatively low absorption capacity. On the other hand, this process is easily reversible, which reduces the energy required for solvent recovery. In the case of chemical absorption, the situation is reversed – the CO<sub>2</sub> absorption capacity is significantly higher, while the desorption process becomes more difficult and requires heating to relatively high temperatures. Therefore, one of the main challenges in CO<sub>2</sub> capture research is finding a balance between capture capacity and the ease of regeneration of the absorption medium. Many of the liquid media studied to date, including DESs and ionic liquids (ILs), exhibit both strong absorption capacity and moderate desorption conditions. **Unfortunately, these solvents, especially ionic liquids, are often very viscous, which reduces the absorption/desorption rate of carbon dioxide.** In the case of DESs, this problem can be solved by adding a third component whose primary function is to reduce the system’s viscosity.

Azolide-based ionic liquids are an example of systems that, although inherently highly capable of absorbing CO<sub>2</sub>, are highly viscous. Mixing these ILs with a hydrogen bond donor can result in the formation of less viscous binary DESs, which often have lower absorption capacity compared to the original IL because the azolide anions can be “trapped” in the strong hydrogen bond networks of such DESs. Hydrogen bond networks appear to switch the reactivity of azolide anions toward carbon dioxide on and off. These ions are characterized by strong basicity, which can cause deprotonation of other DES components, such as alcohols. In this case, the azolide anion may no longer be involved in CO<sub>2</sub> chemical absorption; instead, the carbon dioxide molecule reacts with the deprotonated alcohol. The steric properties of the alcohols –OH groups seem to decide about the absorption mechanism. **Adding a third component to azole-based DESs, such as a second HBD, can both lower viscosity and maintain sufficiently high CO<sub>2</sub> absorption, making the mixture more suitable for efficient carbon dioxide capture.**

Based on these mechanistic insights, this project will aim to provide an innovative outcome by advantage over previously known systems of ternary DES compositions to **(a) maximize reversible chemisorption of CO<sub>2</sub> via alcohol activation and controlled anion basicity and (b) minimize desorption energy.** By using different HBAs and HBDs, we aim to **identify a link between the molecular structures of DES components, the strength and structure of the hydrogen bond network in these solvents, and their CO<sub>2</sub> capture capacity.** In line with the EU’s horizontal policy frameworks promoting sustainable and rational design, the proposed approach to ternary DES systems represents a clear mechanistic innovation (design rules) - integrating control over hydrogen-bond strength, spatial accessibility of the azolide anion, and the role of a “diluting” low-viscosity component within a systematic strategy aimed at simultaneously enhancing CO<sub>2</sub> capacity and reducing regeneration energy.

**We hypothesize** that by controlling the hydrogen bond strength and spatial accessibility in ternary DESs containing:

- 1) azolide salt (HBA), which is active and does not form overwhelming hydrogen bonds with a neutral azole or branched chain alcohol;
- 2) a polyhydric alcohol (HBD<sub>1</sub>) that provides the reactive –OH group that can be deprotonated;
- 3) a neutral azole or branched alcohol (HBD<sub>2</sub>) that contributes to structural tuning (viscosity, H-bond strength) without deactivating the anion

we obtain a tunable DESs group characterized by enhanced CO<sub>2</sub> absorption capacity and reduced absorption enthalpy compared to commonly used monoethanolamine (MEA) solutions, enabling lower regeneration energy and lower viscosity, which results in a higher CO<sub>2</sub> absorption rate.

## 2. The significance of the project

### 2.1. Background and Motivation

One of the main directions of contemporary research is the development of technologies aimed at reducing carbon dioxide emissions. CO<sub>2</sub>, a significant greenhouse gas, is emitted primarily during the production of electricity and heat from the combustion of fossil fuels. Due to the near-atmospheric exhaust gas pressure, post-combustion CO<sub>2</sub> capture technologies based on chemical absorption are most commonly used in power plants. Currently, aqueous amine solutions – specifically a 30% aqueous solution of monoethanolamine (MEA) – are the industrial benchmark for carbon dioxide capture [1]. Sterically hindered alkanolamines, such as aminomethylpropanol (AMP), have also been considered because they require significantly less heat during solvent regeneration compared to MEA, reducing the overall energy cost of CO<sub>2</sub> capture [2]. Generally, aqueous amine systems have several drawbacks, including solvent volatility, degradation, and corrosion of process equipment [3]. Therefore, alternative solvent systems are being sought out that overcome these drawbacks and combine high CO<sub>2</sub> capture efficiency with improved stability and reduced energy requirements. Ionic liquids (ILs) and deep eutectic solvents (DESs) appear to be such environmentally friendly solvents. ILs can be structurally tailored to incorporate basic or nucleophilic groups, enabling high CO<sub>2</sub> selectivity. However, their high cost, viscosity, and potential toxicity hinder large-scale application [4]. DESs, formed by mixing a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD), offer a more sustainable alternative. These eutectic mixtures are typically inexpensive, tunable, biodegradable, and exhibit low volatility and high thermal stability, similar to ILs [5].

Most DESs used for CO<sub>2</sub> capture are based on organic halide salts containing ammonium or phosphonium cations as HBAs, combined with HBDs such as alcohols, phenols, or carboxylic acids. Such systems primarily act as physical absorbers, where CO<sub>2</sub> is captured via weak van der Waals interactions. Therefore, their efficiency under ambient conditions is relatively low, making them unsuitable for removing carbon dioxide from flue gases [6].

To enhance CO<sub>2</sub> uptake, recent studies have introduced reactive functional groups into either the HBD or HBA components of DESs. Most of these studies were dedicated to DESs containing amine groups, which can chemically react with CO<sub>2</sub> to form carbamate species, achieving capacities of 0.4–0.8 mol CO<sub>2</sub> per mol of solvent component [7]. However, amine-based DESs have their drawbacks: high viscosity and the need for high regeneration temperatures (e.g., 100–140°C for choline chloride (ChCl) – MEA system and ~110 °C for monoethanolamine hydrochloride (MEA·HCl) – monoethanolamine (MEA) system) [8,9].

Therefore, new solvents capable of chemically binding CO<sub>2</sub> under milder conditions are highly desirable. A promising development involves anion-functionalized DESs, which exhibit improved carbon dioxide absorption efficiency compared with amine-based systems. Azolide-based DESs fall into this category. Mechanistic studies have shown that azolide anions, due to their strong nucleophilicity, can form reversible carbamate-like adducts with CO<sub>2</sub>, in addition to engaging in van der Waals interactions [10–12].

Moreover, studies by Lee *et al.* and Dikki *et al.* have demonstrated that DESs composed of azolide-based salts and ethylene glycol (EG) capture carbon dioxide through interactions involving both the azolide anion and the polyol component. In aqueous solutions of azole-based DESs, water can also participate in the reaction. As a result, in addition to carbonates, carbamates, carboxylates, and bicarbonates can be formed [13,14]. Nie *et al.* further suggested that carbonates may form through a reaction involving choline cations present in DESs containing azolide-based salts [15]. However, in several studies, the authors indicated that the reaction of polyols with CO<sub>2</sub> is the only one that occurs [16,17]. Nevertheless, despite these findings, the detailed mechanism of CO<sub>2</sub> absorption in DESs based on azolide anions remains insufficiently understood and requires further systematic investigation. Without a doubt, it depends on the effective basicity of the azolide anion and on the activation of the –OH groups, both regulated by the hydrogen bond network and steric factors in the DES.

According to literature reports, binary azolide-based DESs exhibit significant CO<sub>2</sub> capacity, often exceeding that of amine-based DESs and conventional aqueous MEA solutions. Moreover, they enable regeneration at temperatures as low as 70°C, significantly reducing energy costs [16]. However, these mixtures

still face two significant challenges: high viscosity after the absorption process reaching up to 200–500 cP or more, which slows CO<sub>2</sub> diffusion and absorption kinetics, and strong hydrogen-bonding interactions that can hinder the nucleophilicity of azolide anions, limiting their reactivity with polyols [18].

To address these limitations, ternary DESs have recently emerged as a novel design strategy. While binary azole-based DESs and ILs have been studied, the role of a third HBD component in modulating CO<sub>2</sub> binding and release remains underexplored. To our knowledge, only two publications have been published so far on ternary DESs based on azolide salts. Wang *et al.* [17] showed that adding ethylene glycol to tetraethylammonium triazolide ([TEA][Tz]) – triazole (Tz) mixtures causes competition for hydrogen bonding and restores anion reactivity, enabling efficient CO<sub>2</sub> chemisorption. Furthermore, the addition of Tz lowers desorption temperatures, which can reach up to 30°C at appropriate Tz content [17]. Similarly, Chen *et al.* [19] showed that in ternary N,N-diethyl-N-methyl-N-(2-methoxyethyl)-ammonium triazolide ([MOEN221][Tz]) – ethylene glycol (EG) – pinacol (PIN) systems, the steric environment around –OH groups determines whether EG or a bulkier alcohol PIN serves as the primary CO<sub>2</sub>-binding site [19]. In these ternary systems, triazolide salt can provide a reactive anion for chemisorption. The authors postulate that the reaction of CO<sub>2</sub> with ethylene glycol is more favorable. However, they also propose that ethylene glycol not only reacts with CO<sub>2</sub> but can also weaken excessive hydrogen bonding networks, thereby "unblocking" the reactivity of triazolides. Incorporating a branched alcohol in DES offers compelling benefits: while it may slightly reduce the overall absorption capacity, it significantly enhances performance by lowering viscosity and decreasing desorption temperature. Therefore, there are currently no well-established design principles or predictive models that enable rational tuning of their structural and physicochemical properties to achieve both high CO<sub>2</sub> capacity and low regeneration energy. Furthermore, no systematic strategies have been proposed to simultaneously optimize these interdependent parameters within a coherent experimental–computational framework. As a result, the rational design of next-generation ternary DESs capable of combining strong chemisorption, facile regeneration, and low viscosity under mild conditions remains an unmet scientific and technological challenge.

Taken together, these findings indicate that ternary azolide-based DESs represent a highly promising class of materials for post-combustion CO<sub>2</sub> capture. The selection of azolide salts as hydrogen bond acceptors (HBAs) is driven by their strong hydrogen-bonding ability, tunable basicity, and high chemical stability, which collectively enable precise control over both the CO<sub>2</sub> absorption mechanism and the viscosity of the resulting DESs. Polyhydric alcohols are employed as primary hydrogen bond donors (HBD<sub>1</sub>) due to their low toxicity, capacity to form extensive hydrogen-bond networks, and reactivity toward CO<sub>2</sub> upon deprotonation. The incorporation of branched alcohols or neutral azoles as secondary hydrogen bond donors (HBD<sub>2</sub>) is expected to allow fine-tuning of solvent properties – particularly by reducing the CO<sub>2</sub> desorption temperature – thus enhancing both the efficiency and reversibility of the absorption process.

## 2.2. The importance of the project results for the development of a given field and scientific discipline

The proposed research addresses a significant gap in green chemistry and carbon capture by providing a comprehensive understanding of CO<sub>2</sub> absorption mechanisms in ternary azolide-based deep eutectic solvents. These mixtures represent a new generation of environmentally friendly, tunable materials with the potential to replace traditional, energy-intensive absorbents. **Therefore, this project aims to systematically investigate the structure-property relationships governing CO<sub>2</sub> capture in these ternary azolide-based DESs, to identify molecular-level design principles that maximize absorption capacity, reduce regeneration energy, and ensure long-term chemical stability.** The results will significantly advance fundamental knowledge of intermolecular interactions and reaction pathways in complex hydrogen-bonded liquids, contributing to the broader development of sustainable solvent technologies. Furthermore, the outcomes are expected to provide valuable guidelines for the rational design of next-generation CO<sub>2</sub> capture media, thereby strengthening the scientific foundations of physical chemistry, chemical engineering, pharmacy and environmental science.

## 3. Research concept and plan

### 3.1. General research plan

The aim of the proposed research is to develop and understand a new class of ternary deep eutectic solvents based on azolide salts for low-temperature and energy-efficient CO<sub>2</sub> capture. The project integrates

computational design, synthesis, characterization, performance evaluation, and data-driven modelling into a coherent research process, as outlined in Figure 1.

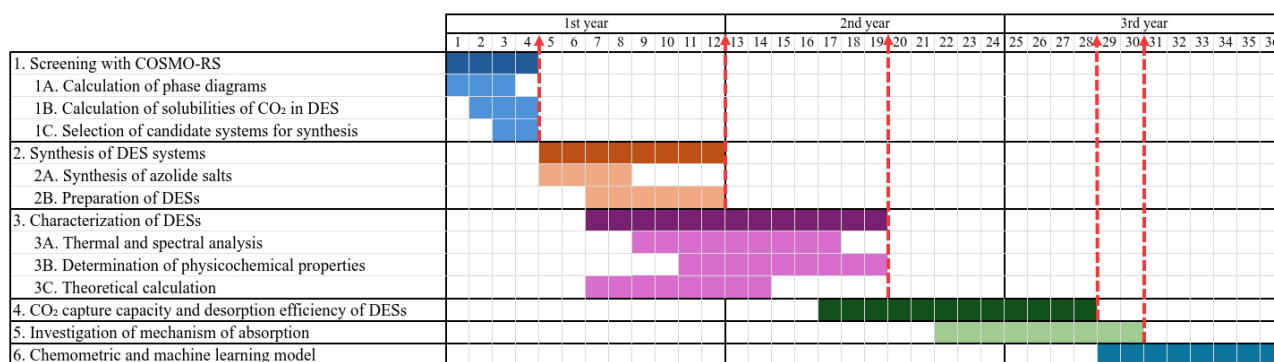


Figure 1 The research plan consists of main phases and sub-tasks. Dashed lines indicate critical points of the project. The project is expected to last for 36 months.

The study will begin with computational screening using the COSMO-RS model to identify optimal combinations of DES components. This predictive approach will minimize costly and time-consuming experimental trials by guiding the selection of hydrogen-bond acceptors (HBAs), primary and secondary hydrogen-bond donors (HBD<sub>1</sub>, HBD<sub>2</sub>), and their optimal ratios. Selected azolide salts will be synthesized and used to prepare ternary DESs, followed by verification of eutectic formation and characterization of molecular interactions. Key physical properties – the water content, viscosity, density, and refractive index – will be measured as functions of temperature. At the same time, molecular dynamics (MD) simulations and DFT calculations will complement experimental data by providing insight into hydrogen-bonding networks and microstructural organization. These results will allow to look for a correlation between DES composition, molecular structure, and macroscopic physical behavior.

Next, computer screening of the synthesized DES efficiency for CO<sub>2</sub> capture will be performed using the COSMO-RS model. For the most promising mixtures, the CO<sub>2</sub> capture performance will then be evaluated through gas absorption and desorption experiments. Measurements of CO<sub>2</sub> solubility, absorption kinetics, and CO<sub>2</sub>/N<sub>2</sub> selectivity will be conducted under controlled conditions, while thermal desorption studies will determine regeneration temperatures and assess long-term stability and reversibility. These experiments will identify DES formulations that combine high CO<sub>2</sub> uptake with low regeneration energy and chemical robustness.

The mechanism of CO<sub>2</sub> chemisorption will be investigated using spectroscopic (<sup>1</sup>H and <sup>13</sup>C NMR) and computational methods to elucidate hydrogen-bonding strengths, carbonate or carbamate formation, and structure–reactivity relationships, clarifying how hydrogen bonding and steric effects govern anion basicity and alcohol activation.

Finally, the experimental and computational results will be integrated into a comprehensive dataset linking DES structure, physicochemical properties, and CO<sub>2</sub> solubility. Using chemometric analyses and machine learning algorithms, predictive models will be developed to identify key structural and property-based descriptors governing CO<sub>2</sub> solubility and selectivity. The combination of structure–property modeling with experimental validation will provide both fundamental understanding and practical tools for guiding solvent design beyond the systems investigated in this project.

## 3.2. Specific research objectives

### 3.2.1. DES component selection using the COSMO-RS model

The initial phase of the research will involve computational screening using the COSMO-RS (Conductor-like Screening Model for Real Solvents) model to guide the selection of deep eutectic solvent (DES) components. COSMO-RS is a computational thermodynamic method that combines quantum chemical surface charge calculations with statistical thermodynamics to predict liquid-phase properties (such as activity coefficients, chemical potentials, solubilities, Henry's law constants, and phase equilibria) of solutes in solvents or solvent mixtures. In this method, each molecule (solute and solvent components) is first treated in a continuum conductor environment to generate a  $\sigma$ -surface (screening charge density distribution) on the molecular surface. These  $\sigma$ -profiles quantify how the molecule's surface interacts with surrounding media. In the next step,  $\sigma$ -profiles are used to compute pairwise interaction energies between molecular surface segments

(via electrostatics, hydrogen-bonding, and van der Waals interactions). From the interactions, one obtains chemical potentials and thus thermodynamic equilibrium properties (e.g., solubility, phase boundaries).

With the use of the COSMO-RS method, a systematic analysis will be conducted on combinations of azolide salts as hydrogen bond acceptors (HBAs), polyhydric alcohols as hydrogen bond donors (HBD<sub>1</sub>s), and branched alcohols or neutral azoles acting as hydrogen bond modifiers to fine-tune the solvent properties (HBD<sub>2</sub>s). COSMO-RS calculations will be used to predict the composition of proposed DES systems that are liquid at room temperature. **These computational predictions will serve as a rational basis for selecting the most promising candidate systems for experimental synthesis and characterization, thereby minimizing the need for extensive trial-and-error experiments.**

Figure 2 provides representative examples of azolide salt cations and anions, considered as HBAs, while Figure 3 shows hydrogen bond donors that will be evaluated for DES formulations within this project.

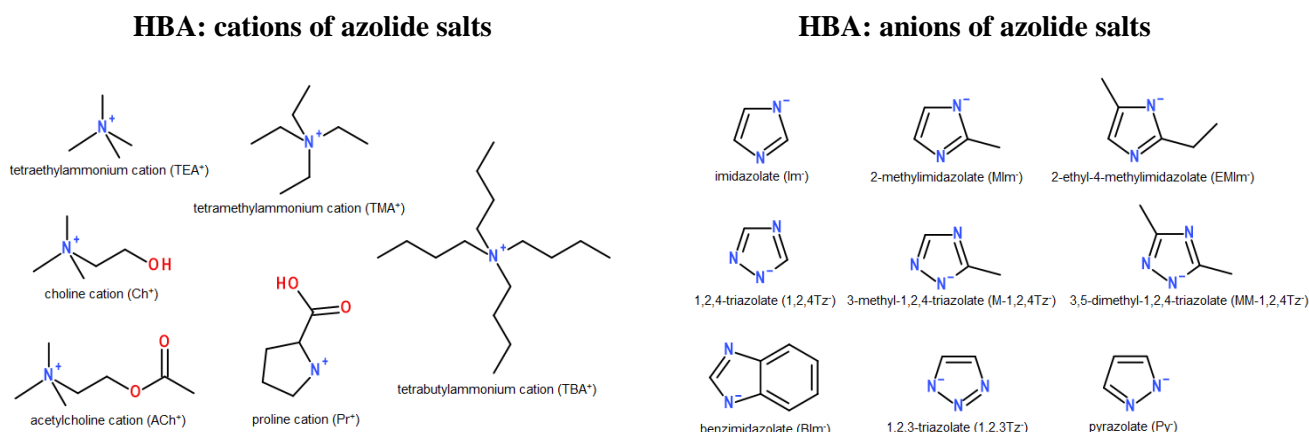


Figure 2 Representative examples of compounds chosen to be HBA components of ternary DESs considered in the project.

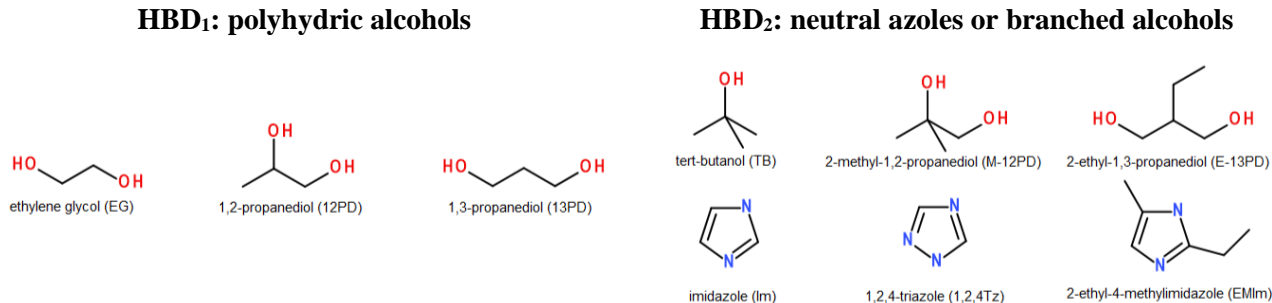


Figure 3 Representative examples of compounds chosen to be HBD components of ternary DESs considered in the project.

### 3.2.2. Synthesis of azolide salts and preparation of deep eutectic solvents

After selecting components of DESs, the synthesis of azolide salts will be performed by reacting alkylammonium or amino acid hydroxides (e.g., proline) with neutral azoles in a 1:1 molar ratio. The synthesis involves the direct mixing of the reagents, which allows for the formation of azolide ions by transferring a proton from the hydroxide to the azole. After thorough mixing, the water produced during the reaction will be removed using a rotary evaporator. The resulting salt will be then dried and used for DES preparation.

Ternary DESs will be prepared by mixing their components in the desired molar ratios and heating them until a room-temperature stable liquid is obtained.

### 3.2.3. Correlating the structure and physical properties of ternary deep eutectic solvents based on azolide salts

The objective of this research task is to establish the relationship between the molecular structure of deep eutectic solvents and their key physical properties relevant to CO<sub>2</sub> absorption processes. Before this stage, verification of eutectic formation will be performed using spectroscopic and thermal measurements. Moreover, the content of water, as a parameter that strongly influences physical properties (especially viscosity), will be measured in DESs. Fourier-transform infrared (FTIR) and <sup>1</sup>H NMR spectroscopy will be employed to

investigate the hydrogen-bonding network and molecular interactions within the DESs. The phase behavior of the studied systems will be characterized using differential scanning calorimetry (DSC) to determine melting transitions and potential glass transition phenomena. The thermal stability of the solvents will also be assessed based on decomposition temperature using thermogravimetric analysis (TGA). Subsequently, macroscopic physicochemical parameters, including viscosity, density, and refractive index, will be measured. Particular attention will be paid to the temperature dependence of these parameters, especially viscosity, which is highly temperature-sensitive. These results will allow us to determine how the composition and structure of the eutectic mixtures – namely, the type and ratio of hydrogen bond donors, including HBD<sub>1</sub> and HBD<sub>2</sub>, and acceptor (HBA) – affect their physical properties. Moreover, intermediate structural data obtained by IR and NMR spectroscopy can be additionally verified by molecular dynamics (MD) simulations and DFT calculation.

#### **3.2.4. Evaluation of CO<sub>2</sub> capture performance**

This task aims to evaluate the potential of synthesized deep eutectic solvent (DES) systems for removing carbon dioxide from gas mixtures with low CO<sub>2</sub> partial pressures. The assessment will be based on precise measurements of CO<sub>2</sub> solubility and absorption-desorption performance under various operating conditions. Quantitative CO<sub>2</sub> absorption and desorption studies will be conducted to determine the efficiency and reversibility of gas capture in the designed DESs, which are predicted to have a strong CO<sub>2</sub> affinity using the COSMO-RS model. Because the overall gas separation efficiency depends on differences in the solubility of the gas mixture components, selectivity is a fundamental performance parameter. Therefore, to calculate the ideal selectivity coefficient for each solvent system, the solubilities of both CO<sub>2</sub> and N<sub>2</sub> will be measured. Gas absorption experiments will be conducted under controlled temperature and pressure conditions, using isochoric and gravimetric techniques. Absorption kinetics and viscosity measurements will provide information on mass transfer and transport limitations that may affect capture efficiency.

Thermal desorption studies will be conducted at temperatures ranging from 30 to 120°C to determine the optimal desorption temperature. To assess long-term operational stability, each DES formulation will undergo at least 5 absorption-desorption cycles. The data obtained will determine solvent stability, reaction reversibility, and operational stability with repeated use, enabling the identification of the most promising formulations for carbon dioxide capture.

#### **3.2.5. Mechanistic characterization – determining how H-bonding and steric hindrance control anion basicity and alcohol activation, using NMR, FTIR, and DFT calculations.**

This task aims to explain the molecular mechanisms regulating CO<sub>2</sub> capture in deep eutectic solvent systems. We will investigate how the HBD<sub>2</sub> steric effect and the strength of hydrogen bonds in DESs influence anion basicity (HBA) and alcohol activation (HBD<sub>1</sub>) – two key parameters controlling CO<sub>2</sub> chemisorption efficiency. To achieve this goal, spectroscopic studies of deep eutectic solvents (<sup>1</sup>H and <sup>13</sup>C NMR, FTIR) will be performed before and after exposure to CO<sub>2</sub>. This data will allow the differentiation of chemisorption and physisorption pathways. Additionally, it will enable the monitoring of hydrogen bond shifts and the identification of carbonate, carbamate, or alkoxide-CO<sub>2</sub> species, giving an insight into the particular pathways in which chemisorption occurs in the studied systems. Most probable chemisorption pathways for a sample ternary system are presented in Figure 4.



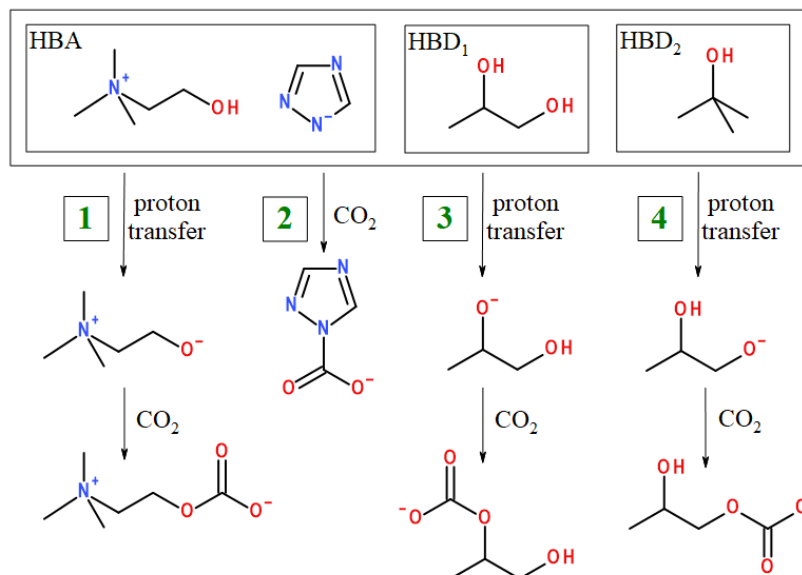


Figure 4 Most probable chemisorption pathways for a sample ternary system.

Furthermore, complementary DFT calculations will enable the quantification of hydrogen bond energies, charge distributions, and enthalpy of reactions associated with CO<sub>2</sub> binding reactions, providing molecular-level insight into the relationship between structure and reactivity of mixtures.

### 3.2.6. Designing models to predict carbon dioxide solubility based on DESs structure and/or their physicochemical properties

The objective of this task is to establish well-defined relationships among the molecular structures of DESs, their physical properties, and CO<sub>2</sub> solubility. By defining these relationships, we can rationally design and screen new DES formulations that optimize CO<sub>2</sub> capture performance. To achieve this, comprehensive datasets will be compiled, including descriptors derived from molecular structure (e.g., hydrogen-bond donor and acceptor types, functional groups, and steric parameters) and experimentally measured physicochemical properties (such as viscosity, density, and hydrogen-bonding strength). CO<sub>2</sub> solubility data obtained in task 3.2.4 will serve as the target variable for model development. Advanced data analysis will utilize chemometric techniques and machine learning algorithms (e.g., regression, decision-tree, and neural network) to identify key structural and property-based predictors of CO<sub>2</sub> solubility. The performance of the models will be evaluated through cross-validation and statistical metrics to ensure robustness and predictive accuracy. The models will provide a quantitative framework that links molecular-level characteristics to macroscopic solubility behavior, facilitating the targeted design of next-generation DESs for energy-efficient CO<sub>2</sub> capture.

## 3.3. Preliminary results

### 3.3.1. Estimation of eutectic temperatures and compositions of sample ternary mixtures using COSMO-RS model.

Using COSMO-RS, phase diagrams for three sample systems were calculated. The systems consisted of 1,2-propanediol (12PD) as HBD1, tert-butanol as HBD2 and choline 1,2,3-triazolide (Ch-123Tz), tetramethylammonium 1,2,3-triazolide (TMA-123Tz) or tetrabutylammonium 1,2,3-triazolide (TBA-123Tz) as HBA. For each ternary system, phase diagrams at a temperature close to the estimated eutectic point and at 300 K were plotted – the results obtained for the system with choline 1,2,3-triazolide, as an example, are presented in Figure 5.

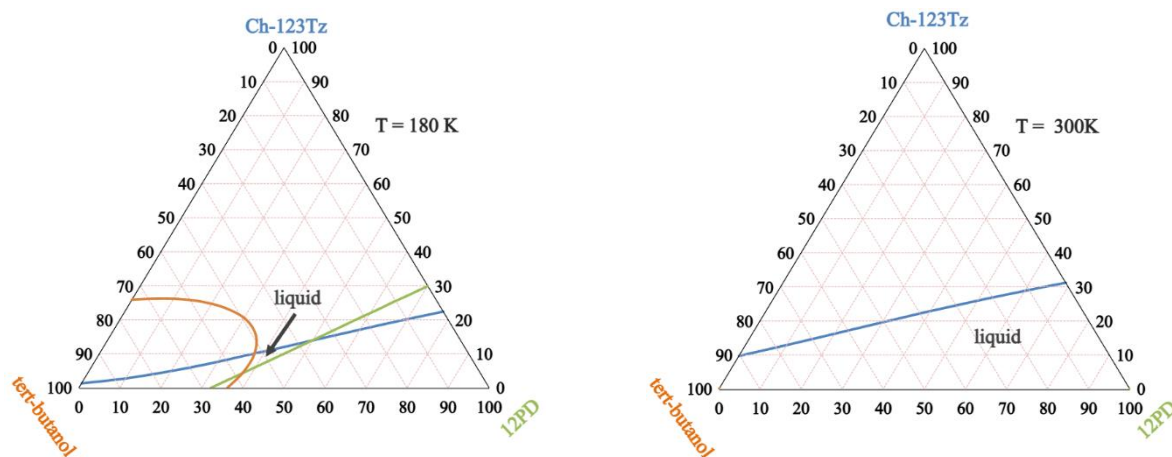


Figure 5 Phase diagrams for a ternary DES system with choline 1,2,3-triazolide at a temperature close to the estimated eutectic point and at 300 K.

According to COSMO-RS calculation, each of three systems considered has a range of compositions in which the system is liquid at 300 K. Additionally, estimated eutectic points are all below the melting temperatures of the components of the ternary systems. It should be mentioned that for the sake of consistency melting points and enthalpies of fusion of all compounds were estimated using COSMO-RS, since there is no experimental data available for some of them.

### 3.3.2. Experimental results

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## 3.4. Risk analysis

**The main objective of the project is to clarify how the secondary hydrogen bond donor (HBD<sub>2</sub>) modulates the properties of deep eutectic solvents (DESs) and the mechanism of their interaction with carbon dioxide.** Preliminary results suggest that ternary DESs based on azolide salts can effectively absorb CO<sub>2</sub>. Regardless of the specific outcomes, the mechanistic insights obtained will significantly enhance our understanding of new solvent materials. Consequently, the project addresses fundamental scientific questions and carries a low risk of failure, as all outcomes, whether positive or negative, will contribute valuable knowledge. A summary of the identified risks and corresponding mitigation strategies is provided below.

**Conceptual risks** are minimal. The study aims to understand the mechanism of a process known to occur in practice. Therefore, any obtained data – whether confirming or contradicting existing hypotheses – will provide valuable information. Unexpected findings will be interpreted as opportunities for expanding mechanistic understanding rather than failures.

**Technical Risks:** Although all experimental and computational techniques have been carefully selected, some methods may prove unsuitable for particular objectives. If this occurs, alternative approaches (e.g., different spectroscopic techniques, complementary analytical methods, or simplified computational models) will be employed. If machine-learning models fail to predict CO<sub>2</sub> solubility with sufficient accuracy, simpler regression-based or mechanistic correlation models will be implemented to ensure the robustness reliability of the predictive framework.

**Logistic Risks:** Certain tasks require access to specialized instrumentation not available daily. If access to such equipment becomes limited, collaboration with external research centers possessing the necessary infrastructure will be established. This flexibility ensures that no significant project delays or data gaps are expected.

**Potential and financial risk** are limited and managed under NCN regulations and university oversight. The most probable issue could be the temporary unavailability of a PhD student. If this occurs, the project timeline will be adjusted in accordance with NCN guidelines. Equipment purchases are planned in the initial project phase to minimize risks associated with price fluctuations. Additionally, the project does not rely on rare or volatile materials, further reducing financial uncertainty.

**Safety Risks** The project involves standard laboratory procedures using mostly low-toxicity substances. For chemicals with higher hazard levels, all experiments will be conducted in accordance with



standard safety protocols, including the use of personal protective equipment and fume hoods. Heating experiments (up to 100 °C) will be performed using regulated equipment with appropriate safety measures. All researchers, particularly early-career participants, will receive detailed safety training before commencing laboratory work.

## **4. Research methodology**

### **4.1. Experimental methods**

#### **4.1.1. Synthesis of deep eutectic solvents**

The synthesis of azolium salts via deprotonation reactions and the preparation of deep eutectic solvents through controlled heating will be carried out by our team using standard laboratory equipment and established procedures.

#### **4.1.2. Spectroscopic characterization and water content determination**

Mid-infrared measurements (FTIR) will be recorded using the Nicolet 8700 IR spectrometer, available at the Department of Physical Chemistry, Gdańsk University of Technology (Gdańsk Tech). Nuclear magnetic resonance (NMR) spectra will be obtained through an external service. Within our university we have a daily access to a NMR service (pay-per-hour or pay-per-spectra payment model).

Water content in the synthesized DESs will be measured by the Karl - Fischer Method using a V10S volumetric Karl - Fischer titrator from Mettler Toledo available at the Department of Physical Chemistry, Gdańsk University of Technology (Gdańsk Tech).

#### **4.1.3. Thermophysical properties measurements**

Phase transition temperatures, including melting and glass transition temperatures of deep eutectic solvents will be determined by differential scanning calorimetry (DSC) using a Star One Differential Scanning Calorimeter from Mettler Toledo. Thermal stability will be evaluated by thermogravimetric analysis (TGA) using a TG 209F3 apparatus from Netzsch Group.

To characterize the physical properties of DESs, our team will determine density, refractive index and viscosity. Measurements will be performed using a DSA 5000 density meter (Anton Paar) and an Abbe refractometer (RL-3, Poland), which are already available in our laboratory. A viscometer adapter will be purchased as part of the project, which will expand our measurements capabilities. Currently, we use the Ubbelohde viscometer for viscosity measurement. However, this device has several limitations, including the need for relatively large sample volumes, extended measurement time, and the inability to accurately evaluate highly viscous samples. Adding a viscometer adapter to DSA 5000 density meter will overcome these limitations, enabling simultaneous determination of density and viscosity over a wide temperature range. Furthermore, this system will require a sample volume more than ten times smaller than that used in current procedures, significantly improving the efficiency and precision of the experiments.

#### **4.1.4. Carbon dioxide solubility**

##### **a) isochoric method**

Carbon dioxide solubility in synthesized eutectic solvents, including their mixtures with water, will be determined using the isochoric method as a function of temperature and pressure, using a set-up constructed at the Department of Process Engineering and Chemical Technology, Gdańsk University of Technology. The system, schematically represented in Figure 6, consists of a gas tank and a chamber (1) equipped with a pressure sensor and a magnetic stirrer (4). Individual parts of the system are separated by gas-tight valves, and the entire system is placed in a thermostatic tank (2), where a constant temperature is maintained by an LS thermostat (Polyscience) with an accuracy of  $\pm 0.25$  K. The water temperature in the tank is measured with a Pt100 sensor. Before the experiment, the vapour pressure of the eutectic mixtures will be determined, and they will be degassed at an elevated temperature and under reduced pressure. An intermediate gas tank (3) will be filled with carbon dioxide (6) and 1 cm<sup>3</sup> of the liquid will be placed in the chamber. Then, a vacuum will be applied using a vacuum oil pump (5). Opening the valve causes the filling of the measuring chamber with gas and initiates the measurement. Pressure is recorded when the equilibrium is reached, i.e., when the pressure in the system stops changing. The amount of the gas absorbed corresponds to the difference between the amount of gas introduced into the measurement system and the amount of gas above the liquid in equilibrium.

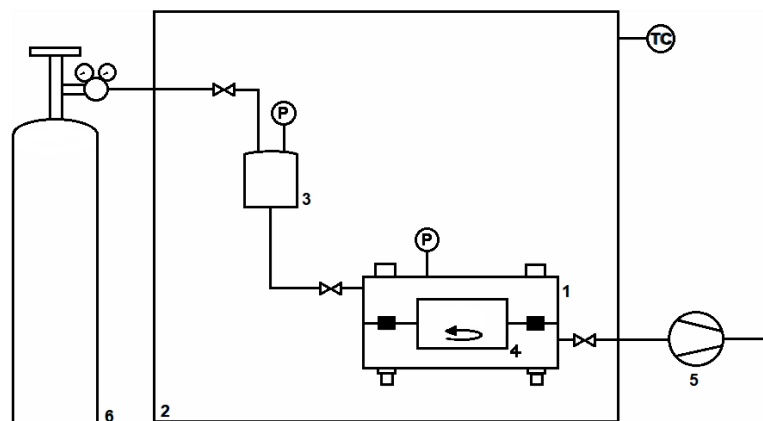


Figure 6 Experimental setup of gas solubility determination (1 – chamber; 2 – thermostatic chamber; 3 – intermediate gas tank; 4 – magnetic stirrer; 5 – vacuum pump; 6 – gas tank)

## b) gravimetric method

Carbon dioxide absorption capacity will be measured gravimetrically using the experimental setup developed for this project (the schematic shown in Figure 7). The setup consists of a gas-tight measuring cell (3) placed in a thermostat bath (2) connected to a gas supply container (1) and vacuum oil pump. In each experiment, 1 ml of DES will be introduced into the measuring cell, which will then be properly sealed and placed in a thermostat water bath. The temperature will be maintained with an accuracy of  $\pm 0.25$  K. Before introducing the  $\text{CO}_2$ , the system will be evacuated using a vacuum pump until the pressure stabilizes, ensuring complete removal of any pre-absorbed gases from the DES sample. Carbon dioxide will then be introduced into the cell. The mass of the cell will be periodically recorded using an analytical balance (RADWAG) with an accuracy of  $\pm 0.1$  mg. Measurements will be continued until the mass remains constant.

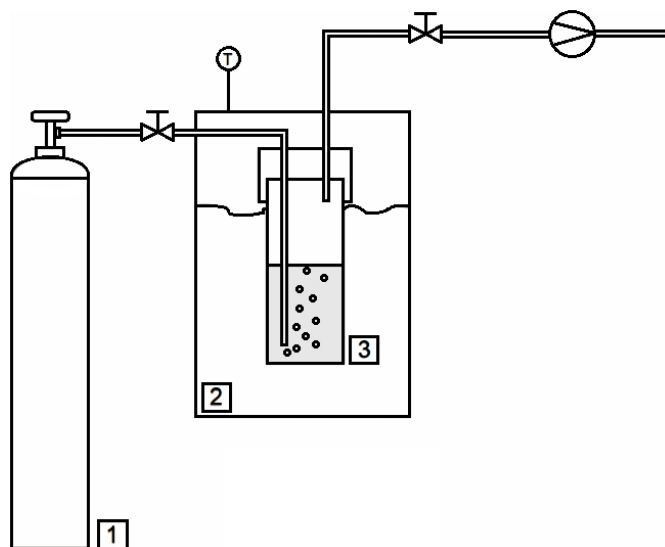


Figure 7 Schematic diagram of the equipment used in the gravimetric method of  $\text{CO}_2$  absorption capacity measurements (1 – gas supply; 2 – thermostatic water bath; 3 – measuring cell).

## 4.2. Computational methods

### 4.2.1. Computational screening using the COSMO-RS model

For the COSMO-RS calculation, software from the Amsterdam Modeling Suite (AMS) will be used. The software is available on the Ares supercomputer in the Academic Computer Center Cyfronet AGH, to which we have access through the PLGrid Infrastructure grant.

### 4.2.2. Theoretical calculations

Theoretical calculations will be carried out using the Gromacs package for MD simulations and the Gaussian for DFT simulations. The software is available at the TASK Academic Computer Center in Gdańsk, where we have an open computational project.

## 4.3. Chemometric and Machine Learning Analysis

All computational analyses using chemometric methods and machine learning algorithms will be conducted in the Python programming environment, utilizing both scripts developed by one of the project investigators (Ph.D. Joanna Grabowska) and open-source libraries for data analysis and advanced statistical modelling. Specialized Python tools and scripts developed as part of the project will be publicly available in a dedicated online repository, ensuring transparency, reproducibility, and reusability in future research.

## 5. Research Team

The Principal Investigator (PI), D.Sc. Dorota Warmińska (ORCID 0000-0002-7070-8288) and the planned project researchers, D.Sc. Marzena Jamróiewicz (ORCID 0000-0002-2637-9886), Ph.D. Joanna Grabowska (ORCID 0000-0002-1074-763X) and Ph.D. Iwona Cichowska-Kopczyńska (ORCID 0000-0003-3070-9603) forms a highly qualified team that can ensure the successful implementation of the project. The research team brings together experts in physical chemistry, spectroscopy, computational modeling, and data analysis, providing a comprehensive skill set essential for the project's multidisciplinary scope. The team members have extensive experience in the synthesis and characterization of deep eutectic solvents, thermophysical measurements, and gas removal techniques (including absorption and membrane methods), particularly in determining the solubility of carbon dioxide using gravimetric and volumetric methods. It is worth noting that D.Sc. Dorota Warmińska supervised the doctoral thesis entitled "Deep Eutectic Solvents – Properties and Application in Carbon Dioxide Separation", highlighting her recognized expertise in this research area. Ph.D. Joanna Grabowska possesses proficiency in molecular dynamics simulations and density functional theory (DFT) calculations, enabling accurate prediction and interpretation of molecular interactions and solubility data. Ph.D. Iwona Cichowska-Kopczyńska is a co-author of a patent concerning a method for purifying gas from volatile organic compounds using an ionic liquid membrane deposited on a porous support. D.Sc. Marzena Jamróiewicz is an expert in the field of thermal and spectral analysis of materials, as evidenced by the numerous research projects she has conducted. Currently she serves as a leader in physicochemical module research devoted to the interactions of polyethylene packaging polymers with oil suspensions that constitute the matrix for already patented medical eye drops. The combined expertise and documented research achievements of the team members guarantee both the reliability of the experimental work and the innovative potential of the proposed methodology. The project will also involve a laboratory technician, postgraduate students, and PhD students, who will gain valuable research experience and bring additional resources to the team. This involvement will further strengthen the team's potential for successful project implementation.

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