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The use of Eutectic Solvents for the enhanced treatment carbon dioxide gas during the absorption of gases related to the oil industries: a review

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Abstract

Global warming is a serious problem caused in part by rising carbon dioxide emissions. Although technologies for capturing carbon dioxide and storing or using it have been developed, they are restricted by the use of hazardous solvents and the formation of dangerous by-products. Research has resulted in the development of non-toxic, efficient, and environmentally friendly solvents. We will look at green solvents used for carbon capture, with a focus on deep eutectic solvents. Temperature, density, and viscosity all influence solvent performance. A few amine solutions in water have been used to absorb GHGs, such as monoethanolamine (MEA). However, they are not environmentally benign. In the wake of research into greener solvents, solvents with high eutectic depth (DESs) have emerged as a unique option. Among the members evaluated hereunder, a DES composed of ChCl/ethylene glycol has an unprecedentedly high gravimetric uptake of 33.7 wt% with good beginning kinetics (25.2 wt% uptakes within 2.5 min) and recyclability. The offered DES also exhibits long-term performance in the presence of water, good resistance to temperature rise, and a relatively low heat of absorption that makes it appealing for regeneration. Even with significant gravimetric uptakes, the DES has considerably less corrosiveness than pure monoethanolamine and ethylenediamine equivalents because of low oxygen/moisture permeability and the hydrogen bonding network that alleviates the corrosion redox cycle. The good qualities found in numerous critical elements of CO2 collection imply that DESs are strong candidates to replace current monoethanolamine-based scrubbing technology and need further investigation. The carbon dioxide absorption in DES has been determined to be adequate for capturing carbon dioxide from flue gases while allowing for quick DES regeneration. It's analogous to ionic liquids at normal temperatures. Nearly 95% of the natural gas generated in Iraq's oil fields remains untapped. To investigate

atmospheric carbon absorption in choline chloride and ethylene glycol at various pressures according to the structural investigation. Instead of collaborating, the anion and the hydrogen bond donor (ethylene glycol) are competing for control of the carbon dioxide interaction. The ethylene glycol–CO2 interaction dominates at lower pressures, whereas the chloride–CO2 interaction takes over as the dominant interaction at higher pressures. Since this discovery, the CO2 absorbent can be employed in the deep eutectic solvent in the same way as ionic liquids do, but a donor can be utilized in the hydrogen bond.

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1. Introduction

The rise in anthropogenic greenhouse gas (GHG) emissions, particularly carbon dioxide (CO_2), that began in it seems likely that the preindustrial past is the primary cause of the present-day climate change. Unusual shifts in the global climate system. A rise in Climate change, sea-level rise, floods, droughts, and rainfall patterns are all factors to consider. Changes can be seen, as well as infectious disorders. The GHG emissions will continue to rise, resulting in long-term climatic effects. are expected to have severe and lasting consequences affecting mankind and ecosystems, by the end of the century, surface temperatures might rise by up to 5 degrees Celsius [1][2]. More than 80% of global CO_2 emissions come from fossil fuels and minerals. climate change, Intended as a statement of the Intergovernmental Panel on Climate Change (IPCC). Emissions of CO_2 are caused by the combustion of fossil fuels, the movement of goods, and ammonia production, iron smelting, and cement making are among the other industrial operations. However, on the other hand, due to increased demand for fossil fuel derivatives in general, according to industry projections, the oil and gas industries will be in high demand once the epidemic is over. The search and development of environmentally appropriate substitutes for the exploration, transportation, and processing of oil and gas continues. and a control of gaseous emissions, especially carbon dioxide, is a fundamental commitment. Hydrates, waxes, absorbs carbon dioxide, asphalt, lumps, naphthetes, scales, erosions, and emulsions are all typical difficulties in petroleum works, and all require distinct chemical solvents to process [3][4]. This rise was attributed to increasing energy demand for heating and cooling as a result of increased worldwide energy consumption as well as meteorological conditions in countries [5][6].

As a result, CO_2 capture and storage (CCS) have emerged as one of the most effective ways of preventing large-scale CO_2 emissions into the atmosphere. CO_2 waste capture, CO_2 transit to a storage facility, and CO_2 storage in a secure location are the three phases of CCS. These efforts have been hindered by the high expense of isolating CO_2 from gaseous sources such as combustion gases, ambient air, and synthetic gaseous sources. capture and storage (approximately US\$ 60 per ton of CO_2) and the lack of progress in recent years. Following combustion, precombustion, oxyfuel combustion, and electrochemical separation are the most often used methods for capturing carbon dioxide (CO_2) [6][7]. Among the currently known technologies for this purpose, The simplest method is post-combustion capture. In the course of a process that makes use of fossil fuels, this equipment is employed to remove CO_2 from the exhaust gasses. Extraction of CO_2 from other gases can be accomplished by a variety of methods including absorption, adsorption, and membrane separation. Once the post-combustion process is completed, CO_2 can be stored or used as a fuel, as seen in Figure 1.[8]



Figure 1. Postcombustion CO₂ capture process[8].

Regeneration uses CO_2 to release CO_2 from the absorber, which raises the temperature and/or reduces the pressure in the absorption. A reversible chemical reaction takes place to capture CO_2 using chemical reagents, resulting in the formation of loosely bound intermediates and a physical absorption process that involves CO_2 being Absorbent columns are then used to extract the solvent that has been physically absorbed [7]. Many drawbacks are linked with absorption. These include, but are not limited to, the corrosion of laboratory equipment and the high energy consumption of solvent regeneration, as well as solvent evaporation losses and solvent degradation in situations with high oxygen concentrations [10].

When it comes to various techniques of capturing CO_2 from flue gases by chemical absorption, it has long been common practice to employ aqueous amine solutions as solvents instead of organic solvents such as monoethanolamine, methyl diethanolamine, and 2-amino-2-methyl-1-propanol [11] [12].

Absorption capacity, reactivity, selectivity, and cost are all advantages of these materials [13]. environmentally unfriendly because of toxicity, partial breakdown, high vapor pressure, and other factors such as corrosion-inducing byproducts, intense energy use, and high uptake costs. This has resulted in cost-effective CO_2 absorbers and collection devices being developed by researchers[14][15]. Ionic liquids (ILs) and deep eutectic solvents (DESs) have gotten a lot of interest as potential replacements for aqueous amine solutions. because of their great thermal and chemical stability, low vapor pressure, and capacity to pick the appropriate ions. When there's a low vapor pressure, the amount of energy needed to regenerate and remove CO_2 is lower. resulting in lower operating costs [16].

Capturing CO_2 has been proposed using ILs [18] and [19]. However, to obtain ILs, several chemical reactions and purification phases are required, all of which raise the price of the solvent. The biodegradability and toxicity potential of some ILs are also factors to consider. Furthermore, their high viscosities limit their application on a large scale in comparison to ordinary solvents [6][15].

These disadvantages may be exacerbated in some cases, depending on the IL precursor elements that were used in their synthesis. It is because of these shortcomings that DESs have become widely accepted as novel CO_2 capture solvents [21][23]. Similar to ILs, they have good heat and chemical resistance, specialization, low vapor pressures, and low vaporization rates. Additionally, DESs have several advantages, including low cost, high biodegradability, an easy preparation method that does not require additional purification, and the ability to synthesize from biodegradable components with little byproduct production [9][23]. It has become increasingly attractive as an alternative solvent for CO_2 capture because of these drawbacks [21][22]. Similar to ILs, they have good heat and chemical resistance, specialization, low vapor pressures, and low vaporization rates. Additionally, DESs have several advantages, including low cost, high biodegradability, an easy preparation method that does not require additional purification [9][24]. Research into DES applications in CO₂ capture technology has led to comparisons of various methodologies and investigations of DES molar ratio effects, changes in gas solubility due to HBA and HBD, as well as differences in DES SO₂ solubility, CO₂, CH₄, and H₂S. As a result of this inquiry According to the updated literature, chlorinated n-butyl triphenolic bromide (BTPB), n-butyl trimethyl methanaminium chloride (TMAC), methyl triphenyl bromide (MTPB), chlorinated dimethylaminoethanol chloride (DEAC), and cholinergic chloride are examples of HBAs used as precursors in the production of DESs. urea, urea dimethylurea, urea N-methyl urea, ethylene urea ethylenurea, trimethylene glycol, ethylene glycol, glycerol amines (ethanolamine, diethanolamine, and triethanolamine), 1,4-butanediol, 2,3-butanediol, 1,2-propanediol, 1,2-propanediol, DESs may be a solution to a variety of challenges in the petroleum sector, including carbon dioxide emissions from burning fossil fuels.

This brief paper explores the history of DES, its current industrial applications, and the potential for using DES as an environmentally friendly solution to the greatest challenge in petroleum extraction and the control of gases emitted from its combustion: the production of gas hydrates. Depending on the source of the gas or oil well, the amount of carbon dioxide in natural gas can range from 4 to 50%. Before being transported, NG must be preprocessed to satisfy the standard pipeline requirements of less than 2% CO_2 , and the gas must have a carbon dioxide level of fewer than 50 ppmv for the liquefaction process [9][10].

2. Solvents For Extreme Eutectic Protection

Eugenic comes from the Greek word for low melting and is used to describe this substance. It can be applied to a liquid or an alloy of metals. In general, Due to carefully calibrated ratios between constituents, a eutectic system consists of elements with the lowest attainable melting temperature when combined. Because they do not have covalent or ionic connections, these components can only interact with one another through intermolecular interactions [9], the following is a timeline of the development of DESs: The first observation of the formation of a eutectic combination of sodium amide and potassium amide was made in 1918 when the history of DESs starts. It was in the 1980s that the exponential increase in the number of research began, and it wasn't until 2003 that DES was introduced as an ionic liquids (ILs) alternative [10.]

DESs have similar traits to ionic liquids as a subclass. Because the cost of the raw ingredients is minimal, it is simple to synthesize DES, and it is also comparably less expensive. Furthermore, DESs are frequently biodegradable and less harmful [6]. But it's important to remember that DESs and ILs differ greatly from one another. A eutectic combination of Lewis or Brnsted acids and bases produces DESs, which contain a variety of anionic and/or cationic species. However, the main components of ILs are a single kind of discrete anion and cation [7]. The hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) for DESs are frequently generated from two or more salts [8,9]. As listed in Table 1, four different types of DES may be created. [13] [14]

Туре	Combination		
Ι	quaternary ammonium salt + metal chloride		
II	quaternary ammonium salt + metal chloride hydrate		
III	quaternary ammonium salt + hydrogen bond		
	donor		
IV	metal chloride hydrate + hydrogen bond donor		

Table 1: Deep eutectic solvents are available in a variety of forms [11].

Although there are several different types of DESs, type III DESs are the most investigated since the availability of a diverse range of hydrogen bond donors suggests that they are versatile [2]. The preparation of DES is simple by the mixing of HBD and HBA at a specific temperature in two ways: (1) when the HBD and HBA are mixed, the lower melting point constituent begins to melt, and then the remaining compound, which has a high melting point, is put into the liquid and the mixtures are melted collectively; and (2) when both constituents are mixed and melt together, since the first work of Abbot et al. 2003 [3]. For example, the solid beginning material of ChCl and Urea was heated at 1:2 proportional to acquire a blend that was liquid at ambient temperature. Numerous DES were prepared, as studied in [4][5], and numerous DES were generated from a liquid at ambient temperature mix made from a solid starting with a mixture of ChCl and Urea that had been cooked at a 1:3 proportionality. The components of the DES molecule are depicted in Figure 2, and how they interact or form bonds with one another throughout the molecule's production is show



Figure 2: Chemical structure of DES type III [12].

DESs have been adopted in a variety of sectors, according to past studies. DESs can be used in a variety of fields, including nanoscale, biodiesel production, photocatalysis, electrodynamics, extraction and separation, polymer synthesis, and related materials synthesis. DESs have various intriguing features that make them a possible choice for green solutions in extraction and extract technologies, biotech, geotechnical sciences, absorption & adsorption, and even wastewater treatment [18] [20].

3. Gas Solubility in Dissipation Measurements (GSM)

Studying Henry's law constant and gas selectivity has also helped researchers understand how gases dissolved in DESs are solubilized [13]. The first investigation into the solubility of CO_2 in a dilute acid solution with choline chloride and urea was carried out at temperatures ranging from 313.15 K to 333.15 K and pressures ranging from 10 to 130 bar. Three parameters were found to influence the solubility of CO_2 in DESs: Three factors influence CO_2 solubility: I) CO_2 pressure; II) temperature; and III) the molar ratio of ChCl/urea [13]. No articles were found in the databases utilized in this investigation between 2009 and 2012. As a consequence, important research findings were returned to numerous groups from 2013 to 2020, as shown shown in Figure 2. For gas separation, one of the most significant qualities is the solubility of the gas.



Figure 3. Journal papers from 2008 to 2020 that looked into CO2 capture with DESs. The databases that were used in the search were Google Scholar, Springer Link, Elsevier [14].

3.1. Comparing IL and DES Gas Solubility

Since 2001, researchers have been looking at the solubility of gases in ILs [15][16][17]. In addition, in 2008, work on determining the solubility of gases in DESs began [18]. Gas solubility in ILs has been demonstrated to occur based on the functional groups of the ILs; absorption can be chemical or physical, and it is generally greater than that of organic solvents [19]. ILs are potential options to trap carbon solvents because they have a low melting point and are quite stable [20]. Unfortunately, ILs have a high viscosity, which can be exacerbated by the creation of intermolecular hydrogen bonds between ILs and CO_2 , resulting in the development of a gel that hinders CO_2 absorption. However, by minimizing the formation of intermolecular hydrogen bonds between ILs and CO_2 capture may be avoided. It is preferable to construct ILs where hydrogen bonds are formed intramolecularly [21].

DESs are a novel type of solvent that is usually less harmful to the environment than traditional solvents. They've been proposed as a replacement for ILs in a variety of processes, including metal extraction and separation. Additionally, alkaline and transition metal ions can be removed from the water when this is accomplished. The absorption of CO_2 from the atmosphere is accomplished through the use of both physical and chemical absorption processes. Exothermic CO_2 dissolution but not spontaneous CO_2 dissolution is observed in DESs, where the enthalpy and entropy of CO_2 are constantly in the negative [22]. It is easier to melt DESs than their ancestors because their melting points are lower. Therefore, DESs with melting points close to room temperature are preferred for gas solubility because they use less energy. However, a DES composed of ChCl/ethylene glycol has an unprecedentedly high gravimetric uptake of 33.7 wt% with good beginning kinetics (25.2 wt% uptakes within 2.5 min) and recyclability [23][24].

Due to their high viscosity, mass and heat transfer are made more challenging in DESs. Water can reduce viscosity but also competes with CO_2 in DESs, reducing the solubility of the gas [25][26]. We then tested the solubility of CO_2 in different DESs as well as ILs and found that choline chloride-based DESs outperformed their counterparts. To check for CO_2 collection in ILs and DESs at temperatures relevant to industry [27], they employed the equation of state for soft statistical associative fluid theory (soft SAFT EoS).

Utilizing cyclic working capacity, regeneration heat, viscosity, diffusivity, and solvent consumption, they assessed these solvents' potential. At 298 K and between 0.001-25 bar of pressure, the solubility was assessed. Technical calculations and under certain situations, To determine the potential of these solvents, it was found that ILs had higher CO₂ absorption (ranging from $x_{CO2} = 0.05$ to 0.50) than all of the DESs tested (ranging from $x_{CO2} = 0.025$ to 0.15), a finding that varies from that of [28][29].

The cyclic working capacity was evaluated at 298 K and pressures of 12 and 27 bar. When the pressure was increased from 10 to 25 bar, all of the solvents examined showed an increase in cyclic working capacity. However, ILs showed a greater rise than DESs (ranging from 20% to 54% for ILs and 33.7% to 45% for DESs). As the pressure climbs from 10 to 25 bar, the CO_2 diffusion coefficient increases, improving mass transfer and absorption. DESs and ILs are incompressible fluids and so do not influence viscosity.

3.2. Gas solubility measurement methods.

Methods for measuring gas solubility in DESs have been varied. When comparing these strategies, the most effective was determined. As an example, we'll have a look at how CO_2 it is possible to determine the solubility in ChCl/urea DES at a 1:2 molar ratio. The Supporting Information for each operation contains all of the technical specifics pertaining to that procedure. Based on the data in Table 2, it is difficult to determine which technique is the best because each one has its own set of pressure and temperature limits, in addition to its own set of advantages and disadvantages. Although calculations of CO_2 solubility are accurate [13][30]. For example, a lower pressure is used, which results in less energy expenditure in the second study.

		Points			
	Ref	Techniques	Positive	Negative	
[13]	•	• Has a good thermal stability	• Low solvent regeneration energy	High viscosity	
		 It has a high polar 			
	•	Non toxic			
	•	High ionic conductivity			
	•	• Non - volatile			
	•	 Has a good thermal stability 			
[31]				• temperature values with low precision	
	•	 High heat capacity 			
	•	Non corrosive	 small sample amount 		
[32]		High heat capacity	 computational data recording 	 Low absorption capacity 	
[33]		• buffer tank	• Low absorption capacity	• Degradation problems in presence of SO ₂ and O ₂ in flue gas	
		 incubation heater 		 corrosion problems 	
		 static stainless steel equilibrium vessel 			
[30]			 Data recording using compute 	• temperature values with low precision	
			• no sampling		
			• small sample amount		

Table 2. CO₂ Solubility in DES Apparatus: Benefits and Drawbacks [30].

3.3. Gas Solubility by an DESs.

Gas solubility is affected by the molar ratio of HBA to HBD donors in DESs, with the majority of instances increasing. The solubility of choline chloride and urea in CO_2 is studied in molar ratios of 1:1.5, 1:2, and 1:2.5 [13].

The greatest CO_2 solubility was found at a 1:2 ChCl/urea molar ratio and 0.309. Because DES is formed at a 1:2 molar ratio, it has the lowest melting point and the molecular connection facilitates gas dissolution [13].



Figure 4. Molar ratio affects CO₂ solubility [34].

Another experiment examining the relationship between the solubility of CO_2 and the molar ratios of DESs and colleagues [35], 1:4 and 1:5 mole ratios, ChCl/methyldiethanol amine at 1:5 and 1:8 mole ratios, TBAB/ethylene glycol at 1:2, 1:3, or 2:1 molar ratios, and TBAB/methyldiethanol amine at 1:2 and 1:1 molar ratios, respectively, was found as well as the effects of chlorination were investigated. Scientists have discovered that raising the

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HBD/HBA molar ratio in DESs results in increased CO_2 solubility in all conditions tested. It was found that increasing the amine composition resulted in increased solubility in the case of glycols and that the rising solubility resulted in increased solubility toward CO_2 in the case of amino acids [35].

The identical effects, as indicated by ChCl/levulinic acid and ChCl/furyl alcohol, are examples of reactions that occur in this paragraph at molar ratios of 1:3, 1:4, and 1:5 when the two chemicals are combined. [23] In particular, it is vital to emphasize that, according to [36], it is uncertain that there is no precise molar ratio at which DES occurs under the conditions described in this paragraph; as a result, the discussion was limited to molecular interactions when a rise in molecular ratio results in increased solubility, which is not always the case. Figure 4 displays the previously described behavior of increased solubility with increasing molar ratio as depicted in the preceding section [32]. CO_2 solubility was examined in ChCl/glycerol at molar ratios of 1:3, 1:7, and 1:8, as well as MTPB/ethanolamine at molar ratios of 1:6, 1:7, and 1:8.

Solubility decreased as a result when HBD was raised in each instance. According to this finding, the physical properties of these DESs cannot be completely attributed to the contribution of the molar ratios of their component components [32]. There has been no solid-liquid equilibrium investigation for the MTPB/ethanolamine combination. However, this has not been confirmed experimentally [37]

3.4. Impact of HBD on the Solubility of Gases.

Gas solubility must take the hydrogen bond donor into account since it directly affects absorption potential. Leron and colleagues [37].[30] [37] When the molar ratio is 1:2 and the pressures are low. The solubility of CO_2 in DESs, including ChCl/urea, ChCl/ethylene glycol, and ChCl/glycerol, was examined. In this case, the relationship between ChCl and glycerol (0.398) is superior to that between ChCl and urea (0.308).

Ethylene glycol, on the other hand, only has two hydroxyl groups, which means that the link between CO_2 and ethylene glycol is weaker than that between urea and CO_2 (Table 3) [38.]

When CO₂ solubility was examined in chlorofluorocarbon (Cl/phenol) and chlorofluorocarbon (ethylene glycol) at a 1:3 molecular ratio, the results obtained [38] were different from those obtained by the authors. This finding reveals that the solubility of the DES composed of phenol is lower than that of the DES composed of ethylene glycol in water.



Table 3. the chemical structures of HBDs [30].

The urea-based DES has less solubility than the ethylene glycol-based DES. According to the study, during carbon absorption, CO_2 has a higher affinity for basic solvents than acidic solvents. Acidity and basicity in nonaqueous fluids are represented by pK_a .

As a result, acidic species have a lower pK_a , while basic species have a higher pK_a . The ethylene glycol pK_a is 14.22 [34], and the urea pK_a is 13.82 [39], according to the pK_a of the HBDs. In part due to the high pKa value of ethylene glycol, this substance has the greatest ability to solubilize the greatest quantity of CO₂ [40]. According to a comparison of ChCl/ethylene glycol and ChCl/trimethylene glycol, the latter has doubled the absorption capacity of the former. This is attributed to the longer alkyl chain, which increases the free radical absorption capability (Table 3). [41]

According to the findings of this investigation, the solubility of CO_2 in chlorinated ethylene glycol and chlorinated trimethylene glycol is the same, indicating that chlorine trimethylene glycol is preferred to chlorinated ethylene glycol in this application. However, they also looked into the solubility of trimethylene glycol in chloroform and phenol, and their findings were comparable to those obtained with trimethylene glycol.

Researchers at the University of California, Berkeley, carried out yet another significant experiment in the 1960s [42][43]. It was discovered that levulinic acid, ACC, TEAC, TEAB, TBAC, and TBAB were all effective HBDs for CO₂ and SO₂ solubilities in DESs when a 1:3 molar ratio of levulinic acid and ChCl was used as the HBA. TEAB/levulinic acid displayed the lowest CO₂ solubility when heated to the same temperature as the other two compounds, but TBAC/levulinic acid demonstrated the highest CO₂ absorption capacity when heated to the same temperature as the other compounds.Rather than the structure of anions in the solution, the action of quaternary ammonium salts on CO₂ absorption appears to be connected to the structure of cations. Because of the extra acetyl ester group present in ACC/levulinic acid DES, the CO₂ solubility of all DESes except ACC/levulinic acid DES is increased. However, this is not true in the case of ACC/levulinic acid DES, which has a lower absorption capacity because of this [44].

3.5. The Effect of HBA on the Solubility of Gases

Due to their greater ability to affect solubility than HBDs, hydrogen bond acceptors are crucial for gas solubility. Ji et al.'s [45] 2016 examined the CO₂ solubility in DESs made of phenol as the HBD and ChCl, TMAC, and TEAC as the HBA at a 1:3 molar ratio. They discovered that CO₂ solubility decreases in the following order: ChCl/phenol > TMAC/phenol > TEAC/phenol. According to the authors, this outcome is brought about by ChCl's greater molecular interaction with CO₂ than it is with TMAC or TEAC (Table 4) since ChCl has one hydroxyl group.

For CO₂ absorption, the authors have so far relied on the length of the alkyl chain as well as the functional groups to determine the optimal HBA[47]. In this research, the solubility of CO₂ in TBPB/phenol and ATPPB/phenol at a 1:4 molar ratio was investigated by combining experimental data with molecular dynamics simulations. Although the effect of HBA type on solubility has been studied in detail, it has been found that the site-to-site radial function has impact distribution (RFD) а stronger on solubility than **HBDs** [48][49]. An exceptionally strong and forceful peak at a 1:4 molar ratio is generated by the reaction of phenol as HBD with chloroform, TMAC, and TEAC as HBA. According to their findings, the solubility of CO₂ declines in the following order: chloroform/phenol > TMAC/phenol > TEAC/phenol (in that order). TMAC and TEAC have a stronger molecular contact with CO_2 than ChCl, which only has a single hydroxyl group, and this is due to the higher molecular contact between ChCl and CO_2 than TMAC and TEAC (Table 4) [49]. The CD•HB peak (CD denotes the CO_2 atom and HB denotes the H atoms in the benzene rings) was seen for the

ATPP⁺ and CO₂ pair, but the CD•••H3/H5/H7 peak (CD•••H3/H5/H7) was observed for the TBP⁺ and CO₂ pair, which was broader and weaker. Due to this difference, the interactions between ATPP⁺ and CO₂ are stronger than those between TBP+ and CO₂, which explains why CO₂ solubility is higher in the ATPPB/phenol DES[47].



Table 4. the molecules of HBAs[49].

3.6. In terms of CO₂ solubility, DESs that are hydrophilic and hydrophobic are contrasted.

The solubility of CO_2 in polar DESs has been extensively studied recently, and this study will discuss that topic. Potential solvents for gas absorption, hydrogen bonding DESs have a significant downside in that they may absorb a large quantity of water during the absorption process, which reduces their mass adsorption efficiency and necessitates a high energy CO_2 desorption phase [50]. According to preliminary findings, hydrophobic DESs appear to be a feasible solution to this problem.

Although it was only recently constructed, the first investigation into CO_2 solubility in these DESs was carried out in [41] and yielded encouraging results [41]. TBAB/decanoic acid, N₈₈₈₁Cl/decanoic acid, N₈₈₈₁-Br/decanoic acid, N₈₈₈₁Cl/decanoic acid, N₈₈₈₁-Br/decanoic acid were all tested between 298.15–323.15 K, and 0.9019 bar to evaluate the CO_2 solubility in each of these solutions.

According to their findings, when compared to other DESs previously published in the literature, the hydrophobic DESs tested to have the highest CO₂ solubility (values ranging between 0.239 and 0.284 mol CO₂/mol of DES), which they attribute to their hydrophobic nature. This DES outperformed some fluorinated ILs in terms of efficacy[50]. At 313.15 K and 1 bar, [50], TETA, and [TEPA]Cl/thymol were used to test the solubility of CO₂ in these solutions. According to the results, the measured values were 1.298 mol CO₂/mol DES and 1.355 mol CO₂/mol DES for the first and second samples, respectively .

Despite the development of new chemical bonds, both DESs retain their hydrophobic characteristics after CO_2 has been absorbed. It is important to note that, although there have only been two studies on gas absorption using hydrophobic DESs published in the literature, the results indicate that these solvents have the potential for CO_2 collection, indicating that additional research in this sector is required.

4. Hydrate inhibitors with deep eutectic solvents

Hydrocarbons are solid addition complexes made composed of a network of water cage molecules that act as both a "host" and may trap light aromatic rings as "guests". Gas hydrate formation is a common occurrence that poses a significant operational and safety concern [56][57]. Chemical inhibition is the most common approach used to prevent hydrate formation [57]. The conventional method of preventing gas hydrates issues in the pipelines is to implement thermodynamic hydrate inhibitors (THIs) injection. The THIs works by moving hydrate equilibrium conditions to higher pressure and lower temperature regions [58][59]. Because DESs contain functional groups capable of making hydrogen bonds, high biodegradability, and low toxicity, as well as low vapor pressure, they have a lot of potentials to be effective THIs [56][57]. The presence of DESs in water-based drilling fluids based on choline chloride, urea, and Shale inhibitors such as to proof that DESs are effective THIs, new compounds such as 3-phenyl propionic acid, a conic acid, and 3-mercaptopropionic acid have been proposed [47].

DESs based on choline chloride showed significant uptake of CO_2 from burning fossil fuels, up to levels needed for piping to avoid hydrate formation [61]. They are a collective group of scholars who have supplied unique data to various projects Hydrocarbon-bearing restrictions in methane hydrates were shown to occur in the following order: Choline chloride, urea DES, and urea ChCl > DES > urea is the order in which these reactions occur. although DES did not outperform plain ChCl. It does demonstrate that DES has the potential to be a thermodynamic gas hydrate inhibitor. Since DESs are often made by combining HBD and HBA, there is a substantial margin for greener hydrocarbon reservoir inhibitors to be utilized. Many compounds have been studied as possible gas hydrate inhibitors, but many have concerns with biodegradability or performance. Mixing compounds to create DESs, on the other hand, could be a good idea [31].

A blend of outside choline chloride and urea, for example, has the extra benefit of each component producing a DES Even Tetraethyl Ammonium Bromide, which is particularly powerful, may be coupled with glycols to form the required DESs. With the same method, a variety of compounds may be used as DES-based gas hydrate inhibitors. The several options for manufacturing effective DESs-based gas hydrate inhibitors have been largely overlooked. After the COVID-19 epidemic has passed, the authors want to see further research into greener techniques in the fuel business [47].

5. Applications in the gas sector

Many other processes and materials have been developed in recent years to replace amine-based CO₂ collection devices, including freshly researched compounds such as DESs. DESs have great adjustable qualities and can be modified for enhanced CO₂ solubility. The open literature in this field has mostly focused on systems including choline chloride, examined for addressing issues connected with the use of DESs as gas absorbents. [52], to create DES-based CO₂ scrubbing systems using imidazolium-based DES and superbase combinations. All dearomatization CO₂ removal procedures are based on the hydrogen bond interaction between DESs and the atoms to be eliminated. In the removal of impurities, the hydrogen bonding characteristics and the delocalization of charge generated by hydrogen bonding are important. Figures 5 illustrate the mechanisms of DES-based dearomatization and CO₂ removal. DESs are employed in the flow assurance industry for the removal of pollutants and improving oil recovery. The development of gas hydrates and pipeline corrosion are just two of the many issues that flow assurance addresses [53][54]. In their rigorous corrosivity analysis, Ullah et al. [55] found corrosion rates of 0.029 mm/year and 0.54 mm/year on CO₂-saturated DES and MEA systems, respectively. This shows that the DESs of cholinium chloride and levulinic acid are excellent options for the prevention of corrosion in fuel pipelines. DESs as gas hydrate inhibitors, on the other hand, have received relatively little research

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Figure 5: Dearomatization of the DES algorithm [56].

6. Discussion.

An analysis of how many articles featured only experimental data revealed that 69% of the publications contained just experimental data, as determined by modeling or both. Furthermore, papers involving modeling are still in the minority, accounting for only 23% of all articles, whereas papers comprising only modeling account for 18% of all publications.

A CO_2 solubility gap in DESs has been discovered as a result of the rarity of publications that contain both experimental data and modeling in the same research, as well as studies that involve thermodynamic modeling using various equations of state. Solubility of CO_2 in DESs was assessed in 67% of the articles that investigated it, with SO_2 solubility being recorded in 22% of the publications. This has resulted in a paucity of research into the solubility of other greenhouse gases (GHGs), which are just as detrimental to the ecosystem as CO_2 and, in some circumstances, even more so than CO_2 . According to this study, further experimental evidence on DES solubility is needed even for CO_2 and SO_2 gases. As previously stated, gas solubility exceeding 40 bar is not well-studied. The capacity (moles gas per kilogram solvent) at a certain temperature and relative pressure of the gas, as well as the related Henry's law constant, are used to define the solubility of various gases in a range of DES.

Keeping in mind that there are an immense number of DESs that can be formed, and even minor details about molecular interactions might be useful in the DES design process, is critical. It is important to note that innovative DESs have the potential to solubilize a substantial amount of gas; for example, hydrophobic DESs have the potential to solubilize more CO_2 than any other DES hitherto examined. However, despite the importance of exploring gas solubility in DESs, the issue can be expanded to include new possibilities and applications for this information. The extraction of crude oil and natural gas can be cost-effective and environmentally benign if DESs are used, for example. Experimental data is required to provide answers to such difficulties. New means for reaching offshore platforms, as well as new hurdles, will be created if DESs are successfully deployed in oil and gas extraction operations.

7. Conclusions and Prospects

In conclusion, was found a family of DESs whose gravimetric CO_2 uptakes far surpass those of the previous DESs and ILs, as well as the conventional scrubbing process. Among the tested HBA-HBD combinations, ChCl/ethylene glycol exhibited the highest uptake of 31.5 wt% after 3 hrs at 30 oC with good initial absorption kinetics (25.2 wt% after 2.5 min) and robust recyclability.

The release of greenhouse gases (GHGs) into the atmosphere by humans elevates the global average temperature and has significant health repercussions. Chemicals such as MEA, MDEA, and AMP are frequently employed in the capture of CO_2 and other gases due to their high absorption capacity. However, because of their toxicity, partial disintegration, and high vapor pressure, these substances aren't regarded as benign by the environmental community. The use of environmentally friendly solvents in carbon capture applications has grown in popularity as a result of their environmentally friendly characteristics. In order to overcome these limitations, DESs have been investigated as new solvents for the collection of greenhouse gases, particularly CO_2 and SO_2 . The eutectic solvents contain a group of features that make them suitable for use in the carbon dioxide absorption process, such as high stability, low cost, and easy manufacturing process.

Deep eutectic solvents (DES) are effective solvents for capturing carbon dioxide and hydrogen sulfide reversibly. They are 'green', that is, environmentally beneficial and low-cost to create. The capacity (moles gas per kilogram solvent) at a certain temperature and relative pressure of the gas, as well as the related Henry's law constant, are used to define the solubility of various gases in a range of DES. The gas solubility grows linearly with pressure but decreases with temperature, indicating that the process is exothermic due to the negative enthalpy of the solution. The carbon dioxide absorption in DES has been determined to be adequate for capturing carbon dioxide from flue gases while allowing for quick DES regeneration. It's analogous to ionic liquids at normal temperatures.

References

- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*, 1, 70–71. https://doi.org/10.1039/b210714g
- [2]. Ali, E., Hadj-Kali, M. K., Mulyono, S., Alnashef, I., Fakeeha, A., Mjalli, F., & Hayyan, A. (2014). Solubility of CO2 in deep eutectic solvents: Experiments and modelling using the Peng-Robinson equation of state. *Chemical Engineering Research and Design*, 92(10), 1898–1906. https://doi.org/10.1016/j.cherd.2014.02.004
- [3]. Alioui, O., Benguerba, Y., & Alnashef, I. M. (2020). Investigation of the CO2-solubility in deep eutectic solvents using COSMO-RS and molecular dynamics methods. *Journal of Molecular Liquids*, *307*, 113005.
- [4]. Alkhatib, I. I. I., Ferreira, M. L., Alba, C. G., Bahamon, D., Llovell, F., Pereiro, A. B., Araújo, J. M. M., Abu-Zahra, M. R. M., & Vega, L. F. (2020). Screening of ionic liquids and deep eutectic solvents for physical CO2 absorption by Soft-SAFT using key performance indicators. *Journal of Chemical & Engineering Data*, 65(12), 5844–5861.
- [5]. Altamash, T., Amhamed, A. I., Aparicio, S., & Atilhan, M. (2019). Combined experimental and theoretical study on high pressure methane solubility in natural deep eutectic solvents. *Industrial & Engineering Chemistry Research*, 58(19), 8097–8111.

- [6]. Anderson, J. L., Dixon, J. K., & Brennecke, J. F. (2007). Solubility of CO2, CH4, C2H6, C2H4, O2, and N2 in 1-Hexyl-3-methylpyridinium Bis (trifluoromethylsulfonyl) imide: Comparison to Other Ionic Liquids. Accounts of Chemical Research, 40(11), 1208–1216.
- [7]. Anthony, J. L., Maginn, E. J., & Brennecke, J. F. (2002). *Gas solubilities in 1-n-butyl-3-methylimidazolium hexafluorophosphate*. ACS Publications.
- [8]. Bates, E. D., Mayton, R. D., Ntai, I., & Davis, J. H. (2002). CO2 capture by a task-specific ionic liquid. *Journal of the American Chemical Society*, 124(6), 926–927.
- [9]. Chen, Y., Ai, N., Li, G., Shan, H., Cui, Y., & Deng, D. (2014). Solubilities of carbon dioxide in eutectic mixtures of choline chloride and dihydric alcohols. *Journal of Chemical & Engineering Data*, 59(4), 1247–1253.
- [10]. Dawson, R. M. C., Elliott, D. C., Elliott, W. H., & Jones, K. M. (2002). Data for biochemical research (Vol. 3). Clarendon press.
- [11]. Dawson, R. M. C., Elliott, D. C., Elliott, W. H., & Jones, K. M. (1969). Data for Biochemical Research Oxford University Press. *New York and Oxford*.
- [12]. Deng, D., Han, G., & Jiang, Y. (2015). Investigation of a deep eutectic solvent formed by levulinic acid with quaternary ammonium salt as an efficient SO 2 absorbent. *New Journal of Chemistry*, 39(10), 8158–8164.
- [13]. Deng, D., Jiang, Y., Liu, X., Zhang, Z., & Ai, N. (2016). Investigation of solubilities of carbon dioxide in five levulinic acid-based deep eutectic solvents and their thermodynamic properties. *The Journal of Chemical Thermodynamics*, 103, 212–217.
- [14]. Dietz, C. H. J. T., van Osch, D. J. G. P., Kroon, M. C., Sadowski, G., van Sint Annaland, M., Gallucci, F., Zubeir, L. F., & Held, C. (2017). PC-SAFT modeling of CO2 solubilities in hydrophobic deep eutectic solvents. *Fluid Phase Equilibria*, 448, 94–98.
- [15]. Energy, G. (2019). CO2 status report. IEA (International Energy Agency): Paris, France.
- [16]. Feng, Z., Jing-Wen, M., Zheng, Z., You-Ting, W., & Zhi-Bing, Z. (2012). Study on the absorption of carbon dioxide in high concentrated MDEA and ILs solutions. *Chemical Engineering Journal*, 181, 222–228.
- [17]. Ghaedi, H., Zhao, M., Clough, P. T., Anthony, E. J., & Fennell, P. S. (2020). High CO2 absorption in new amine based-transition-temperature mixtures (deep eutectic analogues) and reporting thermal stability, viscosity and surface tension: Response surface methodology (RSM). *Journal of Molecular Liquids*, *316*, 113863.
- [18]. Gu, Y., Hou, Y., Ren, S., Sun, Y., & Wu, W. (2020). Hydrophobic functional deep eutectic solvents used for efficient and reversible capture of CO2. *ACS Omega*, *5*(12), 6809–6816.
- [19]. Gurkan, B. E., de la Fuente, J. C., Mindrup, E. M., Ficke, L. E., Goodrich, B. F., Price, E. A., Schneider, W. F., & Brennecke, J. F. (2010). Equimolar CO2 absorption by anion-functionalized ionic liquids. *Journal of the American Chemical Society*, *132*(7), 2116–2117.
- [20]. Haghbakhsh, R., & Raeissi, S. (2017). Modeling the phase behavior of carbon dioxide solubility in deep eutectic solvents with the cubic plus association equation of state. *Journal of Chemical & Engineering Data*, 63(4), 897–906.
- [21]. Haghbakhsh, R., Keshtkar, M., Shariati, A., & Raeissi, S. (2021). Experimental investigation of carbon dioxide solubility in the deep eutectic solvent (1 ChCl+ 3 triethylene glycol) and modeling by the CPA EoS. *Journal of Molecular Liquids*, 330, 115647.
- [22]. Haider, M. B., Jha, D., Marriyappan Sivagnanam, B., & Kumar, R. (2018). Thermodynamic and kinetic studies of CO2 capture by glycol and amine-based deep eutectic solvents. *Journal of Chemical & Engineering Data*, 63(8), 2671–2680.

- [23]. Haider, M. B., Jha, D., Sivagnanam, B. M., & Kumar, R. (2019). Modelling and simulation of CO2 removal from shale gas using deep eutectic solvents. *Journal of Environmental Chemical Engineering*, 7(1), 102747.
- [24]. Hansen, B. B., Spittle, S., Chen, B., Poe, D., Zhang, Y., Klein, J. M., Horton, A., Adhikari, L., Zelovich, T., & Doherty, B. W. (2020). Deep eutectic solvents: A review of fundamentals and applications. *Chemical Reviews*, 121(3), 1232–1285.
- [25]. Hartono, A., Ahmad, R., Usman, M., Asif, N., & Svendsen, H. F. (2020). Solubility of CO2 in 0.1 M, 1M and 3M of 2-amino-2-methyl-1-propanol (AMP) from 313 to 393K and model representation using the eNRTL framework. *Fluid Phase Equilibria*, *511*, 112485.
- [26]. Hirshfeld, F. L. (1977). Bonded-atom fragments for describing molecular charge densities. *Theoretica Chimica Acta*, 44(2), 129–138.
- [27]. Jacquemin, J., Gomes, M. F. C., Husson, P., & Majer, V. (2006). Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric. *The Journal of Chemical Thermodynamics*, 38(4), 490–502.
- [28]. Jacquemin, J., Husson, P., Padua, A. A. H., & Majer, V. (2006). Density and viscosity of several pure and water-saturated ionic liquids. *Green Chemistry*, 8(2), 172–180.
- [29]. Ji, Y., Hou, Y., Ren, S., Yao, C., & Wu, W. (2016). Phase equilibria of high pressure CO2 and deep eutectic solvents formed by quaternary ammonium salts and phenol. *Fluid Phase Equilibria*, 429, 14–20.
- [30]. Jiang, J., Ye, B., & Liu, J. (2019). Research on the peak of CO2 emissions in the developing world: Current progress and future prospect. *Applied Energy*, 235, 186–203.
- [31]. Joback, K. G., & Reid, R. C. (1987). Estimation of pure-component properties from group-contributions. *Chemical Engineering Communications*, *57*(1–6), 233–243.
- [32]. Kamgar, A., Mohsenpour, S., & Esmaeilzadeh, F. (2017). Solubility prediction of CO2, CH4, H2, CO and N2 in Choline Chloride/Urea as a eutectic solvent using NRTL and COSMO-RS models. *Journal of Molecular Liquids*, 247, 70–74.
- [33]. Keyes, D. B. (1928). Handbook of Chemistry and Physics. (Hodgman, Charles D.; Lange, Norbert A.). ACS Publications.
- [34]. Krishnan, A., Gopinath, K. P., Vo, D.-V. N., Malolan, R., Nagarajan, V. M., & Arun, J. (2020). Ionic liquids, deep eutectic solvents and liquid polymers as green solvents in carbon capture technologies: a review. *Environmental Chemistry Letters*, 18(6), 2031–2054.
- [35]. Leron, R. B., & Li, M.-H. (2013). Solubility of carbon dioxide in a eutectic mixture of choline chloride and glycerol at moderate pressures. *The Journal of Chemical Thermodynamics*, *57*, 131–136.
- [36]. Leron, R. B., Caparanga, A., & Li, M.-H. (2013). Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T= 303.15–343.15 K and moderate pressures. *Journal of the Taiwan Institute of Chemical Engineers*, 44(6), 879–885.
- [37]. Li, G., Deng, D., Chen, Y., Shan, H., & Ai, N. (2014). Solubilities and thermodynamic properties of CO2 in choline-chloride based deep eutectic solvents. *The Journal of Chemical Thermodynamics*, 75, 58–62.
- [38]. Li, X., Hou, M., Han, B., Wang, X., & Zou, L. (2008). Solubility of CO2 in a choline chloride+ urea eutectic mixture. *Journal of Chemical & Engineering Data*, *53*(2), 548–550.
- [39]. Li, X., Kersten, S. R. A., & Schuur, B. (2016). Extraction of guaiacol from model pyrolytic sugar stream with ionic liquids. *Industrial & Engineering Chemistry Research*, *55*(16), 4703–4710.
- [40]. Li, Y., Huang, W., Zheng, D., Mi, Y., & Dong, L. (2014). Solubilities of CO2 capture absorbents 2ethoxyethyl ether, 2-butoxyethyl acetate and 2-(2-ethoxyethoxy) ethyl acetate. *Fluid Phase Equilibria*, 370, 1–7.
- [41]. Lide, D. R. (2004). CRC handbook of chemistry and physics (Vol. 85). CRC press.

- [42]. Lin, C.-M., Leron, R. B., Caparanga, A. R., & Li, M.-H. (2014). Henry's constant of carbon dioxideaqueous deep eutectic solvent (choline chloride/ethylene glycol, choline chloride/glycerol, choline chloride/malonic acid) systems. *The Journal of Chemical Thermodynamics*, 68, 216–220.
- [43]. Liu, F., Chen, W., Mi, J., Zhang, J., Kan, X., Zhong, F., Huang, K., Zheng, A., & Jiang, L. (2019). Thermodynamic and molecular insights into the absorption of H2S, CO2, and CH4 in choline chloride plus urea mixtures. *AIChE Journal*, 65(5), e16574.
- [44]. Liu, X., Gao, B., & Deng, D. (2018). SO2 absorption/desorption performance of renewable phenolbased deep eutectic solvents. *Separation Science and Technology*, *53*(14), 2150–2158.
- [45]. Liu, X., Gao, B., Jiang, Y., Ai, N., & Deng, D. (2017). Solubilities and thermodynamic properties of carbon dioxide in guaiacol-based deep eutectic solvents. *Journal of Chemical & Engineering Data*, 62(4), 1448–1455.
- [46]. Lu, M., Han, G., Jiang, Y., Zhang, X., Deng, D., & Ai, N. (2015). Solubilities of carbon dioxide in the eutectic mixture of levulinic acid (or furfuryl alcohol) and choline chloride. *The Journal of Chemical Thermodynamics*, 88, 72–77.
- [47]. Luo, X. Y., Fan, X., Shi, G. L., Li, H. R., & Wang, C. M. (2016). Decreasing the viscosity in CO2 capture by amino-functionalized ionic liquids through the formation of intramolecular hydrogen bond. *The Journal of Physical Chemistry B*, 120(10), 2807–2813.
- [48]. Luo, X., Guo, Y., Ding, F., Zhao, H., Cui, G., Li, H., & Wang, C. (2014). Significant improvements in CO2 capture by pyridine-containing anion-functionalized ionic liquids through multiple-site cooperative interactions. *Angewandte Chemie*, 126(27), 7173–7177.
- [49]. Lydersen, A. L., Greenkorn, R. A., & Hougen, O. A. (1955). *Estimation of critical properties of organic compounds by the method of group contibutions*. University of Wisconsin.
- [50]. Malik, A., Dhattarwal, H. S., & Kashyap, H. K. (2021). Distinct solvation structures of CO2 and SO2 in reline and ethaline deep eutectic solvents revealed by AIMD simulations. *The Journal of Physical Chemistry B*, 125(7), 1852–1860.
- [51]. Martins, M. A. R., Pinho, S. P., & Coutinho, J. A. P. (2019). Insights into the nature of eutectic and deep eutectic mixtures. *Journal of Solution Chemistry*, 48(7), 962–982.
- [52]. Mirza, N. R., Nicholas, N. J., Wu, Y., Mumford, K. A., Kentish, S. E., & Stevens, G. W. (2015). Experiments and thermodynamic modeling of the solubility of carbon dioxide in three different deep eutectic solvents (DESs). *Journal of Chemical & Engineering Data*, 60(11), 3246–3252.
- [53]. Mulliken, R. S. (1955). Electronic population analysis on LCAO–MO molecular wave functions. I. *The Journal of Chemical Physics*, 23(10), 1833–1840.
- [54]. O'Neill, S. (2020). Global CO2 emissions level off in 2019, with a drop predicted in 2020. *Engineering* (*Beijing, China*), 6(9), 958.
- [55]. Pelaquim, F. P., Barbosa Neto, A. M., Dalmolin, I. A. L., & Costa, M. C. da. (2021). Gas solubility using deep eutectic solvents: review and analysis. *Industrial & Engineering Chemistry Research*, 60(24), 8607–8620.
- [56]. Phani Kumar, P., Paramashivappa, R., Vithayathil, P. J., Subba Rao, P. V, & Srinivasa Rao, A. (2002). Process for isolation of cardanol from technical cashew (Anacardium occidentale L.) nut shell liquid. *Journal of Agricultural and Food Chemistry*, 50(16), 4705–4708.
- [57]. Pires, J. C. M., Martins, F. G., Alvim-Ferraz, M. C. M., & Simões, M. (2011). Recent developments on carbon capture and storage: an overview. *Chemical Engineering Research and Design*, 89(9), 1446– 1460.
- [58]. Ramdin, M., de Loos, T. W., & Vlugt, T. J. H. (2012). State-of-the-art of CO2 capture with ionic liquids. *Industrial & Engineering Chemistry Research*, 51(24), 8149–8177.

- [59]. Ribeiro, B. D., Florindo, C., Iff, L. C., Coelho, M. A. Z., & Marrucho, I. M. (2015). Menthol-based eutectic mixtures: hydrophobic low viscosity solvents. ACS Sustainable Chemistry & Engineering, 3(10), 2469–2477.
- [60]. Salehi, H. S., Hens, R., Moultos, O. A., & Vlugt, T. J. H. (2020). Computation of gas solubilities in choline chloride urea and choline chloride ethylene glycol deep eutectic solvents using Monte Carlo simulations. *Journal of Molecular Liquids*, 316, 113729.
- [61]. Salleh, Z., Wazeer, I., Mulyono, S., El-blidi, L., Hashim, M. A., & Hadj-Kali, M. K. (2017). Efficient removal of benzene from cyclohexane-benzene mixtures using deep eutectic solvents–COSMO-RS screening and experimental validation. *The Journal of Chemical Thermodynamics*, 104, 33–44.
- [62]. Sarmad, S., Mikkola, J., & Ji, X. (2017). Carbon dioxide capture with ionic liquids and deep eutectic solvents: a new generation of sorbents. *ChemSusChem*, *10*(2), 324–352.
- [63]. Sarmad, S., Nikjoo, D., & Mikkola, J. P. (2020). Amine functionalized deep eutectic solvent for CO2 capture: Measurements and modeling. *Journal of Molecular Liquids*, 309, 113159. https://doi.org/10.1016/j.molliq.2020.113159
- [64]. Schmelz, W. J., Hochman, G., & Miller, K. G. (2020). Total cost of carbon capture and storage implemented at a regional scale: northeastern and midwestern United States. *Interface Focus*, 10(5), 20190065.
- [65]. Shahbaz, K., Baroutian, S., Mjalli, F. S., Hashim, M. A., & AlNashef, I. M. (2012). Densities of ammonium and phosphonium based deep eutectic solvents: Prediction using artificial intelligence and group contribution techniques. *Thermochimica Acta*, 527, 59–66.
- [66]. Shukla, S. K., & Mikkola, J.-P. (2018). Intermolecular interactions upon carbon dioxide capture in deepeutectic solvents. *Physical Chemistry Chemical Physics*, 20(38), 24591–24601.
- [67]. Shunji, K., Xizhou, S., & Wenze, Y. (2020). Investigation of CO2 desorption kinetics in MDEA and MDEA+ DEA rich amine solutions with thermo-gravimetric analysis method. *International Journal of Greenhouse Gas Control*, 95, 102947.
- [68]. Silva, L. P., Martins, M. A. R., Conceição, J. H. F., Pinho, S. P., & Coutinho, J. A. P. (2020). Eutectic mixtures based on polyalcohols as sustainable solvents: Screening and characterization. ACS Sustainable Chemistry & Engineering, 8(40), 15317–15326.
- [69]. Sohaib, Q., Vadillo, J. M., Gómez-Coma, L., Albo, J., Druon-Bocquet, S., Irabien, A., & Sanchez-Marcano, J. (2020). CO2 capture with room temperature ionic liquids; coupled absorption/desorption and single module absorption in membrane contactor. *Chemical Engineering Science*, 223, 115719.
- [70]. Solubility of CO2 and CH4 in sterically hindered amine-based deep eutectic solvents. (2020). *Separation and Purification Technology*, 248, 117055.
- [71]. Song, Z., Hu, X., Wu, H., Mei, M., Linke, S., Zhou, T., Qi, Z., & Sundmacher, K. (2020). Systematic screening of deep eutectic solvents as sustainable separation media exemplified by the CO2 capture process. ACS Sustainable Chemistry & Engineering, 8(23), 8741–8751.
- [72]. Soriano, A. N., Doma Jr, B. T., & Li, M.-H. (2008). Solubility of carbon dioxide in 1-ethyl-3methylimidazolium tetrafluoroborate. *Journal of Chemical & Engineering Data*, 53(11), 2550–2555.
- [73]. Sun, S., Niu, Y., Xu, Q., Sun, Z., & Wei, X. (2015). Efficient SO2 absorptions by four kinds of deep eutectic solvents based on choline chloride. *Industrial & Engineering Chemistry Research*, 54(33), 8019–8024.
- [74]. Ullah, R., Atilhan, M., Anaya, B., Khraisheh, M., García, G., ElKhattat, A., Tariq, M., & Aparicio, S. (2015). A detailed study of cholinium chloride and levulinic acid deep eutectic solvent system for CO 2 capture via experimental and molecular simulation approaches. *Physical Chemistry Chemical Physics*, 17(32), 20941–20960.

- [75]. van Osch, D. J. G. P., Parmentier, D., Dietz, C. H. J. T., van den Bruinhorst, A., Tuinier, R., & Kroon, M. C. (2016). Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents. *Chemical Communications*, 52(80), 11987–11990.
- [76]. Wang, J., Cheng, H., Song, Z., Chen, L., Deng, L., & Qi, Z. (2019). Carbon dioxide solubility in phosphonium-based deep eutectic solvents: an experimental and molecular dynamics study. *Industrial & Engineering Chemistry Research*, 58(37), 17514–17523.
- [77]. Zhang, Y., Ji, X., & Lu, X. (2018). Choline-based deep eutectic solvents for CO2 separation: Review and thermodynamic analysis. *Renewable and Sustainable Energy Reviews*, 97, 436–455.
- [78]. Zubeir, L. F., Held, C., Sadowski, G., & Kroon, M. C. (2016). PC-SAFT modeling of CO2 solubilities in deep eutectic solvents. *The Journal of Physical Chemistry B*, 120(9), 2300–2310.
- [79]. Zubeir, L. F., Lacroix, M. H. M., & Kroon, M. C. (2014). Low transition temperature mixtures as innovative and sustainable CO2 capture solvents. *The Journal of Physical Chemistry B*, 118(49), 14429– 14441.
- [80]. Zubeir, L. F., Van Osch, D. J. G. P., Rocha, M. A. A., Banat, F., & Kroon, M. C. (2018). Carbon dioxide solubilities in decanoic acid-based hydrophobic deep eutectic solvents. *Journal of Chemical & Engineering Data*, 63(4), 913–919.