

Review

Deep Eutectic Solvents Feasibility in Oil and Gas Processing Field for Contaminated CO₂ Control

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Abstract: Carbon dioxide capture and storage (CCS) is highly expected to be mitigating the discharges of carbon dioxide in a surrounding environment. Solvents are an integral part of CCS. So far, several solvents have been explored the interest of meeting the requirements such as accessibility, non-harmfulness, biocompatibility, recyclability, and inexpensiveness. However, most solvents face failure in fulfilling the requirements due to many factors, so, this review paper gives a brief discussion about another category of solvent, an analogue of ionic liquids (ILs) named deep eutectic solvent (DES). Extensive research has been done on DES in recent years because of their various attractive advantages, i.e., non-poisonousness, biodegradability, cheap cost and easy preparation, that make them as a promising green solvent for many industrial procedure and application, for instance, polymer synthesis, biodiesel treatment, green chemistry, electrochemistry etc. Therefore, this manuscript mainly focusses on CO₂ capturing through DES in oil and gas field. In addition, the preparation and chemical structures of this novel solvent (DES) is also discussed. Moreover, a detailed study based on experimental solubility of CO₂ in DESs is also reported in this article.

Keywords: Carbon dioxide capture; Deep eutectic solvents; Ionic liquids.

1. Introduction

As the requirements of modern civilisation have been increasing rapidly, the industries continuously produce to meet the demands. As a result, a large amount of CO₂ is released from industries, for example, the production of cement and lime, sugar from sugarcane,

and the combustion of coal, and natural gas. Every year 3 billion tonne CO₂ is added to the atmosphere. Nevertheless, the releasing of coal gas from the production process is one of the utmost greenhouse gas emission, which plays an important role in global warming resulting in urban smog, acid rain and bad impact on human life [1]-[2]. In the preceding decade, CO₂ capture and storage (CCS) from oil & gas has been assumed as one of the pertinent methodologies. The use of alkanolamine in the absorption process of CO₂ is investigated by several researchers. The cost-effective methods of CO₂ capturing by utilising new absorbents provide a possible solution to overcome the greenhouse effect up to some extent. DES is a feasible solvent in green chemistry, that has an optimistic approach in the oil and gas field when comparing with the currently available conventional solvents. Augmentation of CO₂ concentration in the atmosphere because of human exercises is accepted to be one of the fundamental reasons, which can cause an unnatural climate change [3]. On account of its unfavourable impact on the surrounding environment, rural life and also fiscal implications of climate crisis or climate warms, resources have been expended to diminish the emanations of harmful gases such as tetrafluoromethane and other ozone-depleting substance along with CO₂ [4-5]. It has been observed during the last decade that the environmental CO₂ concentration extended from 350-403 ppm; which indicates the impermissible increment in comparison to the previous 20 decades [3-6]. There are four major origins of carbon dioxide discharge. (1) Manufacturing process (2) consumption of fossil energy in heat and electricity plants, (3) the feedstock of hydrocarbon as a source of hydrogen gas manufacturing (4) exudation of CO₂ from vehicles [5]. Numerous methodologies have been implemented for CO₂ capture from the sources of producing electricity from fossil energy. To name a few, membrane, adsorption, physiochemical absorption and cryogenic are some of the highly implemented procedures for CO₂ capture [7]. The absorption process is observed as the most encouraging technology; it is beneficial as compared to adsorption, cryogenic and membrane processes regarding cost and CO₂ catching performance [7-8]. Recently, alkanolamines have caught the attention and mostly used for CO₂ capture [9]-[11]. However, drawbacks have appeared by using Alkanolamines industrially, such as being harmful, inflammable, un-green and causing corrosion [12]-[15]. ILs have been paid special consideration as a substitution to a conventional method, due to their ability to tune their physicochemical properties and hence their liking for CO₂ molecules by choosing the appropriate ions [16], [17]. Though ILs have also revealed a few drawbacks concerning their application for carbon capture purposes, for example, their high viscosity or their cost, which have thwarted their use for capturing purposes at the industrial scale [18-19]. However, these disadvantages are not supposed to be a reason to stop the progress towards attainable CO₂ capture. Many alternatives have been suggested to sustain the design of ILs while keeping away their notable problems. Moving toward green solvents technology, DESs were presented for many applications. Mainly, DESs have been recognised as a viable solvent in comparing with conventional solvent in term of physicochemical properties such as environmentally friendly, high biocompatibility, inexpensive, easy to synthesis, low volatility [20-21]. In this sense many researchers have been stressed on the extensive variety of applications of DES in various field, such as for instance biodiesel synthesis, synthesis of polymers related materials, and different branch of chemistry especially,

electrochemistry, analytical chemistry, physical chemistry and CO₂ capturing technology [22–26]. There are enormous articles have been published on DESs contribution in the given fields since 2003. The goal of this review is to exhibit the possible and beneficial usage of DESs for contaminated CO₂ capturing in petroleum and gas industry and also the investigations of DESs regarding their physical properties, chemical properties, applications, chemical structure, preparation and lastly experimental solubilities CO₂ were accounted and compared in this work, which showed DESs feasibility over conventional solvents. It is hoped that in future, DES will show better performance in oil and gas fields.

2. Deep eutectic solvents

The expanding requests for environmentally friendly procedures inside the system of green chemistry and acknowledgment of phenomenal and favourable features of DESs have led, in the previous twenty years, to a developing enthusiasm for utilisation of these blends as substitutes to conventional organic solvents and their procedure ionic liquids (IL) in various fields. Based upon green chemistry, deep eutectic solvent may be assumed as an adaptable substitute to ILs because of their excellent properties, for instance, non-volatility, reliability, cheap cost and high biocompatibility [20–27]. DESs are usually prepared by mixing of two or three cheap components, that may have the ability to make hydrogen interactions to form a eutectic mixture, because of interaction, the melting point lower than that of every individual component. DES is supposed to be an aqueous state at a temperature lower than 100°C [27]. The concept of deep eutectic solvents was first elucidated by Abbot et al. [28]. Based on mixing of choline chloride (HBA) and urea (HBD) with 1:2 molar ratio and the melting point was 12°C [28] ILs vary from DESs in three major perspectives, firstly, ionic liquids are costly, and some of them exhibit high poisonousness, just as having poor biodegradability, feasibility. On the other hand, DES are inexpensive, biocompatible and environmentally friendly. Another embodiment is the preparations procedures of ILs. Also, DESs are varied somewhat, the preparations of DESs are achieved by blending of two or more constituent, which produce no waste and not needed to be purified, while ILs are tough and costly as well. Lastly, ILs are comprised totally of ions, which interact by ionic bonds; however, DESs contain both ionic and neutral species [29]. Having set themselves up over the most recent few decades, as helpful and regarded as a substitute to fluid and traditional solvents, the potential applications of DES have been broadly investigated. For instance, Xiang et al. (2015) have utilised choline chloride and urea-based DES system for Fe₂O nano spindles [30]. Gu et al. examined the utilization of DESs choline chloride (ChCl) and glycerol (GL) in the transesterification of oilseed rape to generate biodiesel [31]. Likewise, Hayyan et al. used ChCl-based DESs as an additive for producing biodiesel from acidic crude palm oil [32]. Also, the proficiency of deep eutectic solvents in CO₂ Capture technology has been explored. Not long ago, García et al. revealed a density functional theory simulations report on moderation of CO₂ through modern DESs at the molecular level [21]. Moreover, the vast number of experiments and hypothesis were done in the applications of DESs in CO₂ capturing technology [33–34]. The physiochemical characteristics of DESs were investigated by various researchers all around the world, because of, their favourable applications are good industrially [20–27]. Sirat et al. elucidated the physical entities of manganese (II) use as the basis DESs [35]. Furthermore,

another researcher explored the physical features of triglycol as (HBD) with the five mixture of phosphonium and ammonium salts as (HBD) based DESs [20]. On the other hand, many researchers have investigated the toxicity of deep eutectic solvent, and it was discovered that DESs are ordinary, not harmful. Hayyan et al. recently examined the toxicity of choline chloride (HBD) based DESs with four hydrogen donors (HBD), namely, glycerin, ethylene glycol, tri ethylene glycol and urea, the tested DESs revealed as innocuous [36]. Additionally, Huang et al. figured out the harmfulness test on Hydra Sinensis. ChCl and urea-based DESs, it exhibited that DESs could be less damaging as compared to each component [37]. DESs are getting a viable option for both ionic liquid and conventional solvents. It depends upon many factors, but the most significant is the physicochemical properties.

3. Preparation and chemical structure of DESs

In general, the chemical structure of solvents is very essential in deciding their interaction to various solutes. However, when it comes to DESs, minimal investigations have been on the microscopic agents which may influence the structure and characteristics of the DES. In other words, the connection and intermolecular interaction of hydrogen bond donor and hydrogen bond acceptor which have a critical effect on the properties have not been explored [21]. At the beginning period, with respect to this research, there were less accessible research papers in the literature examining the intermolecular structure of the constituents of hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). Very recently, Aissaoui et al. determined the properties of various glycols such as diglycol and triglycol by the help of COSMO-RS [38]. The study indicated the further possibility of hydrogen bonding that occurred during the formulation of new solvent. Furthermore, Abbot et al. and Perkins et al. have explained the interactions of DESs [28–39]. In another study, Zang et al. examined choline chloride and magnesium chloride hexahydrate based DESs, by applying DFT method to explore the stable key structure of molecules in DES. On the hand, the right design of DES and to reasonably grow their application, the complete comprehension of the physical properties is important.

The preparation of DES is simple by the mixing of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) at a specific temperature in of 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 [28]. For example, the solid beginning material of ChCl and Urea were heated at 1:2 proportional to acquire a blend that was liquid at ambient temperature, numerous DES prepared, as studied in [40–41]. Figure 1 represents components in DES and how it interacts or make the bond with one another during the formation of DES molecule. Moreover, it is found that humidity can significantly impact on the properties of DES. Hence, it is profoundly imperative to keep HBAs, HBDs, and the prepared DES away from the vapour or steams. It is supposed to be noticed that the homogeneous mixture of liquid is the ending stage of the procedure of Deep eutectic solvent preparation.

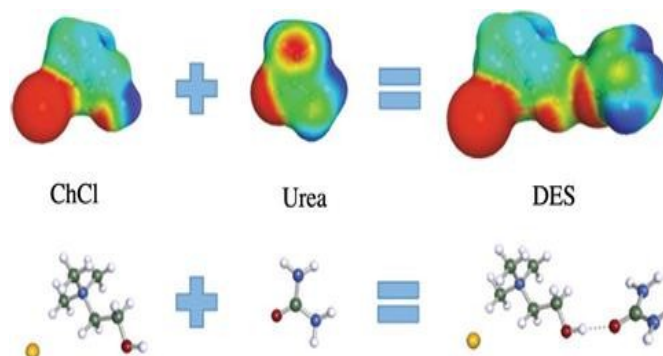


FIGURE 1. Chemical structure of Reline Constituted type III DES [42].

Abbot et al. divided DES into three various groups through its general equation as shown in Table (1) [43].

Table 1. This is a table that represents various classes

Class I : quaternary ammonium salt + metal chloride	(Y = MCl _x , M = Zn, Sn, Fe, Al, Ga)
class II : quaternary ammonium salt + metal chloride hydrate	Y = MCl _x · yH ₂ O, M = Cr, Co, Cu, Ni, Fe
class III : quaternary ammonium salt + hydrogen bond donor	Y = R ₅ Z with Z = -CONH ₂ , -COOH, -OH
class IV : metal chloride hydrate + hydrogen bond donor	

Later, class IV DES also described which comprised inorganic chloride, for instance, Iron (II) Chloride blended with glycols and acetamide group HBD_s [20–44].

4. Potential application of DESs for CO₂ capture in oil and gas technology

The consistent increment of the discharging of carbon dioxide from the combustion of non-renewable energy sources is prognosticated to make huge impact on the worldwide atmosphere [45]. To approach this defiance, the reasonable alternative to manage carbon dioxide releasing is CCS. Usually, there are three ways to deal with CO₂ discharge from power plants: (1) to capture CO₂ from the releasing sources or burning products, (2) transporting the captured CO₂ by vehicles etc. (3) infusing CO₂ underground, to improve oil recuperation or saline water or coal mine [45,46]. There are different processes through CO₂ is captured, but the easiest way which is to be applied as a post-combustion sequester [47]. That incorporates the elimination of pernicious gases like CO₂ from exhaust gases [20], that originates from the burning compartment of the generating station [48]. Various other technologies for post-combustion CO₂ are used, for example, hydration formation, chemical absorption, membranes, metal frameworks

[4-5]. The chemical absorption was considered as economical in post-combustion method [49]. The other techniques are reported to be less suitable in post-combustion [7]. Chemical absorption procedure for CO₂ used was based on reacting sorbent exothermically with CO₂ in the existence of gas flow at ambient temperature [5]. Chemical absorption processes with liquid alkanol amine solution have been used for decades so that the dismissal CO₂ from waste gases stream [50]. Though, applying alkanol amines showed drawbacks industrially, for example, formed salt, corrosiveness, high cost, non-biocompatible etc. [51]. Because of these disadvantages, the researchers started to investigate novel solvents to overcome the existence issues with low cost. Therefore, a new solvent called deep eutectic solvents extensively known as potential substitutes to ILs and conventional solvent [52]. Due its viable characteristics, for instance, accessibility, harmless, non-combustibility, cheap cost, recyclability and biocompatibility [33], DES has been deemed suitable to be applied in CCS technology [24].

5. Investigational dissolubility of CO₂ in DESs

Even though there are various surveys which have been convened to find out the dissolving power of CO₂ in DESs, the CO₂ dissolubility in DESs has been reviewed no long ago [53]. For instance, Adeyemi et al. (2017) very recently, investigated the solubility of CO₂ in the presence of three amine-based DESs, (ChCl-MEA), (ChCl-DEA) and (ChCl-MDEA. This study described the solubility of nominated DES at the various molar ratio, 1:6, 1:8 and 1:10; it is indicated that the solubility of CO₂ increased as the molar ratio of amine in DES increase [54]. Furthermore, Kamgar et al. reported the dissolubility of many various gases, CO₂, CO, CH₄, H₂ and N₂ in Choline Chloride/Urea as a DES, by various ratio molar ratios (1:1.5, 1:2.0 and 1:2.5) and temperature extending from 308K and 333K at pressures up to 5 MPa is resolved. This study indicated the CO₂ solubility in the presence of Choline Chloride to Urea based DES [55]. Furthermore, Lu et al. measured CO₂ dissolubility in Reline : levulinic acid (C₅H₈O₃) based DESs, it is revealed selected DESs dissolubility at distinct temperatures, (303.15 up to 333.15 K) at 0.6 MPa by fix volume saturation way [56], the result of the selected (C₅H₈O₃)-based upon DESs showed better performance for CO₂ capturing as compared to furfuryl alcohol-based upon DES. it is likewise discovered that CO₂ dissolution in DESs expended as expending both pressure and molar ratio of levulinic to Choline Chloride or diminished with increasing the temperature. In another study, measured CO₂ dissolution in ternary DESs comprising of ChCl and dihydric alcohols (consisting, butanediol (BD), Butane-2,3-diol, by 1:2 molar ratios of ChCl (HBA) and dihydric alcohol (HBD) of 1:3 and 1:4 at different temperatures ranging from 293.15 K, 303.15 K, 313.15 K, and 323.15 K under 0.6 MPa pressure by way of an isochoric saturation. Henry's constants and thermal behavior or thermodynamics properties, for example, Gibbs free energy, enthalpy and changes in the entropy of CO₂ preservation were determined from vitro data. The outcomes from this study demonstrated that the CO₂ dissolubility in DESs increment with diminishing temperature and expending pressure, furthermore, DESs consisted of CC and 2,3-butanediol at 1:4 molar ratio exhibited the excellent uptake potential dissolubility of CO₂ across all DESs [57]. Furthermore, Mirza et al. elucidated CO₂ dissolubility's in the presence of three DESs as Reline at 1:2 molar ratio, choline chloride and

ethane-1,2-diol (CH_2OH)₂ at 1:2 molar ratio and choline chloride, dicarboxylic acid ($\text{C}_4\text{H}_6\text{O}_5$), and ethane-1,2-diol (CH_2OH)₂ at 1.3:1:2.2 molar ratios at a distinct temperature ranging from 35.85 to 55.85 C and at 1.6 Bar pressures. In the same order, in this investigation, Henry's constant, Gibbs free energy and both enthalpy and entropy dissolution reveal the CO_2 absorption is exothermic as the internal energy decreases, thereby of gas absorption [58]. However, Xie et al. revealed that how water impact on Reline (ChCl: urea) with ratio 1:2 at operational temperature dimension ranging from 35.05C, 45.05C and 55.05C, and pressure from 6 bar to 45 Bar. It has proven the influence of moisture content on DES. Result indicates that the solubility of CO_2 decreases as the water vapour increase, yet, water vapor can also effect on viscosity of the selected species [59]. On the other hand, carbon dioxide (CO_2) separation is assumed significantly as an energy-saving and CO_2 emission reduction.

In recent years, Francisco et al. formed a new DES based on solvents from lactic acid (HBD), ChCl (HBA) for CO_2 separation. Moreover, the selected DESs physical features were elaborated briefly. The result of this work demonstrated the newly solvent has low solubility of CO_2 compared to other mentioned in literature [60]. Throughout the search directed in this work, it had been remarked that from the years 2009 to 2012 no analysis was performed for CO_2 solubility in deep eutectics solvent. Although, an article was issued by Su et al. in 2009, which aimed was to figure out the CO_2 solubility with blend solvent of 1-aminomethanamide and choline chloride [61]. which indicated the highlight of intriguing research that is the utilising of amine in blending framework to get ready the DESs for CO_2 capture. As far as we possibly know, the first previously revealed article treating CO_2 dissolvability in Reline, by varying molar ratios 1: 1.5, 1: 2 and 1: 2.5, also thermally reading from 313.15, 323.15 to 333.15 Kelvin and 30 Bar pressure was noted. It was indicated that the internal temperature and pressure of the system may affect CO_2 dissolubility in the blends, as expending the pressure, expending the CO_2 solubility. Furthermore, the dissolubility of CO_2 in DES reduced as reducing the degree of hotness and coldness at all pressures, also noted the internal energy of the system was negative at all states. In addition, there is some survey which indicate the CO_2 dissolubility in DESs which have caught attention dramatically within the three years.

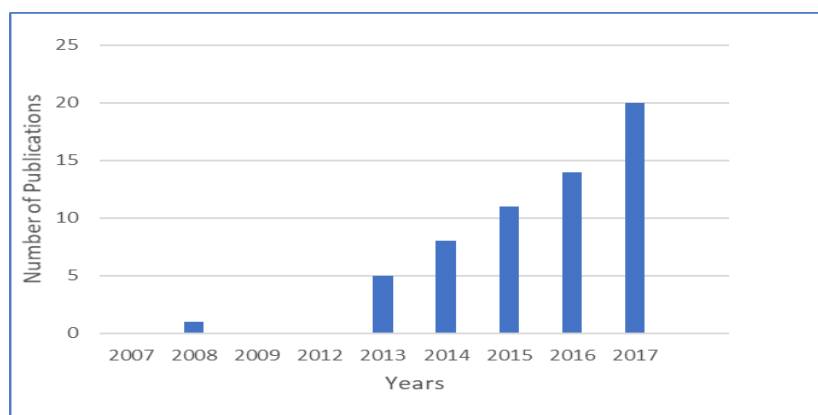


Figure 2. Numbering of articles exploring CO_2 capturing using DESs in the period 2008 to 2017.

From the Figure (2), it is evident that most articles have been published in DESs after the first published article in 2008 by Lu et al. which revealed the dissolubility of utilising DES in CO₂ capturing to explore the variable of solubility. On the other hand, it is demonstrated that there was no publication over four years from 2009 to 2012. In contrast the given figure further represents drastically increased in the number of published articles over three years duration from 2013 to 2017. Deep eutectic solvents have caught great attention in almost every field, due to its flexible properties, for instance, biocompatibility, inexpensiveness, readily available, easy to prepare, ecological delicacy and recyclability. Besides, DESs have a low melting point, low viscosity and have an excellent capability for CO₂ capturing. Due to these the favourable features of DESs, many researchers have been investigated various kind of DESs as showing exceptional performance as compared to conventional solvents. The investigated DESs are in specified Table (1).

Table 1. Dissolubility of CO₂ in various Deep eutecticsolvents.

Variable parameters for CO ₂ dissolubility in different DESs						
Hydrogen bond accepters (HBA _s)	Hydrogen bond donors (HBD _s)	Molar Ratio	T(k)	P(MPa)	mCO ₂	Years / References
Choline chloride (ChCl)	Monoethanolamine	1:6	313.15	0-6	0.3 mol/g	2020 [62]
ChCl	Diethanolamine	1:8	313.15	0-6	0.16	
ChCl	Methyl diethanolamine	1:10	313.15	0-6	0.02	
MEA	Tetrabutyl Ammonium Bromide	1:4	303.15	10.46	0.30-0.106	2020 [63]
	Benzyltriethyl ammonium Chloride	1:4	303.15	10.07	0.24- 0.100	
EAE	Tetrabutyl Ammonium Bromide	1:4	303.15	09.93	0.22-0.071	
	Benzyltriethyl ammonium Chloride	1:4	303.15	10.19	0.24- 0.09	
ChCl	Diethanolamine	5wt%-40wt%	276.15	15	0.146	2020 [62]
Choline Chloride	Lactic acid	2:1	348.15	19.27	0.0248 mol/mol	2013 [64]

Benzyltriphenylphosphonium chloride	Glycerol	1:12	298.15	10 bars	0.0511	2015 [35]
n-Butyltriphenylphosphonium bromide	Ethane-1,2-diol	1:12	298.15	10 bars	0.0503	
ChCl	Monoethylene amine	1:10	313.15	1 bar	0.35	2017 [54]
ChCl	Diethylene amine	1:10	313.15	1 bar	0.18	

Table 1. cont.

Variable parameters for CO ₂ dissolubility in different DESs						
Hydrogen bond accepters (HBA _s)	Hydrogen bond donors (HBD _s)	Molar Ratio	T(k)	P(MPa)	mCO ₂	Years / References
ChCl	Carbamide	1.1.5	332.15	0.5	0.6	2017 [55]
ChCl	Carbamide	1:2.5	332.15	0.5	0.3	
ChCl	Carbamide + water	1:2 + (0.0185)	308.2 +	4.376	0.169	2014 [59]
ChCl	Carbamide + water	1:2 + (0.910)	308.2	4.504	0.151	
ChCl	Carbamide + water	1:2 + (1.83)	308.2	4.499	0.143	
ChCl	Carbamide + water	Reline(0.00%)in water	303	1 bar	5.2	2009 [61]
ChCl	Carbamide + H ₂ O	Reline(86.2%)in water	303	1 bar	17	
ChCl	Carbamide + H ₂ O	Reline(99.10%)in water	303	1 bar	27	

These given tables exhibited the solubility of CO₂ in many different DESs but most of DESs used as CO₂ dissolubility are choline chloride and reline based and their solubility by increasing their amount of concentration. In addition, the following chemical species are investigated as DESs based for the first time in existing literature for carbon dioxide capture and storage. It also demonstrated that DES can be good alternative to ILs.

6. Conclusions

This review article sums up the influential physiochemical properties of DESs and their application for CCS operations. DESs are a novel generation solvent just like the ILs, but with some varying properties. The most important segment of this paper, which is all about DESs preparation and chemical structures indicated the main factors that influence DESs. Although, the available literature on CO₂ gas solubility is confined, the literature study shows better viability of CO₂ solubility in DESs in comparison with the conventional solvents. On the other hand, significant outcomes have been discovered all around by several researchers, that DESs is known as a viable green solvent with good performance CO₂ capture. The progress shown in Figure 2 is a good sign for the possibility of implementing DES for industrial practices involving contaminated CO₂ control in near future. It is highly recommended for the researchers to focus more on DES and utilise the properties for greener applications.

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