

Review Article

Review on Carbon Dioxide Absorption by Choline Chloride/Urea Deep Eutectic Solvents

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In the recent past few years, deep eutectic solvents (DESs) were developed sharing similar characteristics to ionic liquids but with more advantageous features related to preparation cost, environmental impact, and efficiency for gas separation processes. Amongst many combinations of DES solvents that have been prepared, reline (choline chloride as the hydrogen bond acceptor mixed with urea as the hydrogen bond donor) was the first DES synthesized and is still the one with the lowest melting point. Choline chloride/urea DES has proven to be a promising solvent as an efficient medium for carbon dioxide capture when compared with amine alone or ionic liquids under the same conditions. This review sheds light on the preparation method, physical and chemical characteristics, and the CO₂ absorption capacity of choline chloride/urea DES under different temperatures and pressures reported up to date.

1. Introduction

The increased emission of CO₂ from fossil fuel burning is an alarming issue causing severe environmental pollution. This has urged the global community to work toward the mitigation of climate change associated with CO₂ pollution. It is well known that most proven mature technology for CO₂ capture currently is the chemical absorption using aqueous amine solutions due to its relatively low costs, high efficiency, and satisfactory absorption capacity. Nevertheless, this technology has major drawbacks that are mainly significant in the energy consumption during the solvent regeneration step. In addition, amine solutions have several disadvantages such as degradation, evaporation, hydrocarbon coabsorption, corrosion, foaming, and fouling all leading to high overall capture cost [1].

Recently, deep eutectic solvents have been considered as promising solvents to improve CO₂ capture efficiency and to reduce capture cost [2]. Abbott and coworkers introduced the term of “deep eutectic solvent” in 2003 [3]. They got this name from the idea of synthesizing liquids from a mixture of two high melting-point solid raw materials. Deep eutectic solvents (DESs) can be basically defined as a mixture of a

hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) which can bond with each other to form a eutectic mixture having a final melting point that is lower than the melting point of the raw materials (HBD) and (HBA), separately [4].

DESs are typically less expensive, nontoxic, biodegradable, and more synthetically accessible than most ionic liquids. The preparation of DESs could be as simple as mixing constituent components under mild heating, requiring no further purification steps [1].

A very common example of a DES is the mixture of choline chloride and urea which is also named as reline for shortness. Choline chloride has a melting point of 302°C and urea's melting point is 133°C. The mixture melting point is 12°C for a molar ratio 1:2, respectively [4]. In this DES mixture (reline), cholinium chloride is used as the hydrogen bond acceptor (HBA) because of its low cost, low toxicity, biodegradability, and biocompatibility. Urea, on the other hand, is the hydrogen bond donor (HBD) [5].

Although the research in the area of the utilization of DES for CO₂ capture is premature, among the relatively few studies that reported different combinations of DES for CO₂ absorption, those DESs based on choline chloride have

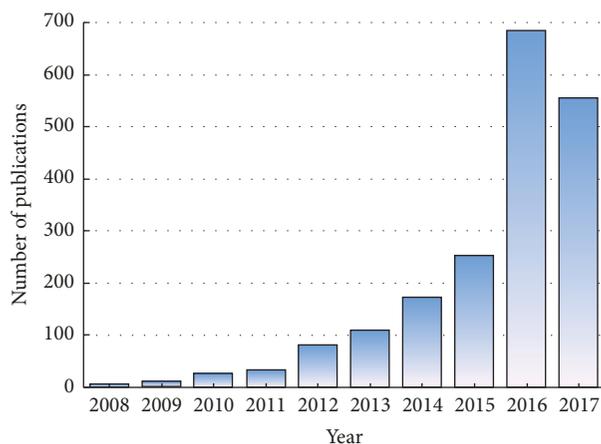


FIGURE 1: Number of publications that contained “deep eutectic solvents” in their titles, keywords, and/or abstracts as obtained from Scopus. Data for the year 2017 are up to May 2017.

proved to be the most efficient ones so far. Therefore, a growth of interest in the research in the field of deep eutectic solvents has been noticed recently as shown in Figure 1.

In this review paper, we will shed light on the synthesis of choline chloride-urea synthesis, characteristics, and their efficiency to capture CO_2 . This is because this mixture has the lowest melting point reported when it is in the ratio 1 choline chloride : 2 urea and has shown high CO_2 absorption capacity at mild conditions [11]. Moreover, we shall summarize the factors that affect CO_2 solubility in this DES and what makes it as a promising solvent for CO_2 capture via absorption technologies.

2. Preparation of Choline Chloride/Urea DES

Deep eutectic solvents can be prepared by two different methods: the heating method and the grinding method [5]. The heating method (the most commonly used in literature) is based on mixing the two components (the HBA and the HBD), which are then heated at around 100°C under constant stirring until a homogeneous liquid is formed. The grinding method, on the other hand, has been largely explored in the preparation of DESs for pharmaceutical purposes and consists of mixing the two components and then grinding them in a mortar with a pestle at room temperature until a homogeneous liquid is formed (Figure 2) [5].

Choline chloride is an organic compound and a quaternary ammonium salt. It has a choline cation with chloride anion, while urea is a cloudless organic compound that is highly soluble in water. Figure 3 shows the chemical structure of choline chloride and urea, respectively.

The preparation of choline chloride/urea deep eutectic solvents is rather simple. Abdullah and Kadhom [4] prepared choline chloride with urea in the molar ratio of 1:2. First, choline chloride was dried at 65°C under vacuum for 24 hr to get rid of any possible moisture. Then urea was added and the mixture was heated at 80°C with continuous stirring until homogeneous colorless liquid was formed. Finally, the DES



FIGURE 2: Preparation of deep eutectic solvents via grinding method [5].

mixture was dried at 80°C and left under vacuum overnight in order to eliminate any possible moisture before characterization. Mirza et al. [8] prepared choline chloride/urea in 1:2 molar ratio by combining the appropriate ratios of solid precursors and then heating the mixture mildly at 70°C overnight until it formed a clear, single phase solution. Florindo et al. [5] prepared dry and wet choline chloride/urea DES. First they dried choline chloride in a high vacuum pump at 40°C for at least 2 days, while urea was used without further purification. For the preparation of the dried samples, the DESs were maintained for at least 4 days in a Schlenk under high vacuum (about 10^{-1} Pa) at room temperature, while for the water-saturated samples, the DESs were maintained for one month in contact with air [5].

3. Characterization of Choline Chloride/Urea DES

Very few studies have been reported on the use of computational methods to investigate choline chloride/urea DES properties at the nanoscopic structure. Sun et al. [17] performed molecular dynamic (MD) simulations to investigate in detail the structural characteristics of mixtures of choline chloride and urea with different urea contents by performing molecular dynamic (MD) simulations and offered possible explanations for the low melting point of the eutectic mixture of choline chloride and urea with a ratio of 1:2. They found out that the insertion of urea molecules caused a change in the density distribution of cations and anions around the given cations significantly. They have also reported on the hydrogen bond lifetimes which indicated that the ratio of 1:2 between choline chloride and urea is critical for a reasonable strength of hydrogen bond interaction to maintain the low melting point of the mixture of choline chloride with urea [17].

Several works have been reported on the chemical and physical properties of choline chloride/urea (1:2) experimentally as summarized in Table 1.

Moreover, the thermal stability of choline-based DES was studied by Rengstl et al. [18] who reported that the decomposition temperature of these solvents is in the range of $269\text{--}290^\circ\text{C}$ which is higher than those reported for ionic liquids [11].

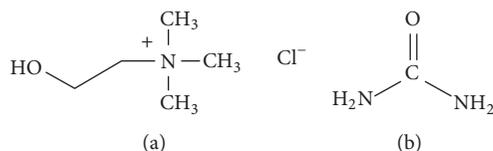


FIGURE 3: Chemical structure of (a) choline chloride structure [6] and (b) urea [7].

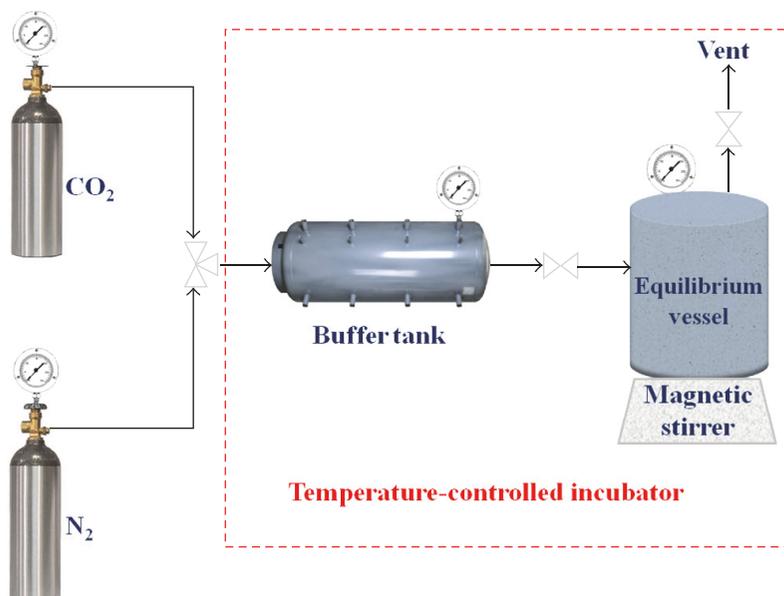


FIGURE 4: Simplified schematic of the vapor-liquid equilibrium setup to measure CO₂ solubility in DES (adopted with modification [8]).

TABLE 1: Physical and chemical properties of choline chloride/urea 1:2.

Property	Value	Reference
Melting point (K)	285.15	[3]
Viscosity at 303 K (mPa·s)	449	[12]
	152	[3]
Density (g/cm ³)	527	[2]
	1.26	[4]
	1.24	[13]
	1.25	[12]
	1.212	[14]
	1.979	[15]
	1.1893	[15]
Surface tension at 298 K (mN/m)	1.1887	[2]
	1.20	[16]
Surface tension at 298 K (mN/m)	52	[12]

4. Measurement of CO₂ Solubility in Chlorine Chloride DES

The measurements of CO₂ solubility in DESs are typically performed with the utilization of a vapor-liquid equilibrium (VLE) setup as shown in Figure 4. The VLE setup usually consists of a buffer tank with a top mounted pressure gauge,

a temperature-controlled incubator, and a static stainless steel equilibrium vessel fitted with a pressure gauge. The equilibrium vessel is provided with valves at the inlet and outlet to control the gas flow.

To perform the experiments of measuring CO₂ absorption, a known mass of the DES is loaded into the equilibrium vessel. The vessel is purged with nitrogen gas and then incubated in a thermally controlled setup for 2 h at the desired experimental temperature. To insure uniform temperature inside the vessel, the system is continuously stirred. After 2 h, the vessel is pressurized to the desired level using pure carbon dioxide gas delivered from the buffer tank. The system should be kept under vigorous stirring at the experimental temperature and the equilibrium point can be reached once the pressure reading of the vessel remains constant for at least 3-4 h [8]. In order to calculate the initial and final concentration of CO₂, it is assumed that the vapor phase consists only of carbon dioxide since the DES has low vapor pressure and can be neglected. Based on this assumption, using the initial and final (equilibrium) pressure readings of the equilibrium vessel, the initial and final concentrations of carbon dioxide can be calculated using the following equation:

$$\Delta n_{\text{CO}_2} = \frac{\Delta PV}{RT}, \quad (1)$$

where Δn_{CO_2} is CO₂ moles absorbed in DES (mol), ΔP is the change in pressure from initial value to the equilibrium

pressure (kPa), V is the volume of equilibrium vessel (m^3), T is the temperature (K), and R is the universal gas constant ($8.314 \text{ J/mol}\cdot\text{K}$).

It is constantly reported that the solubility of CO_2 in the DES increases as the pressure increases and decreases as the temperature increases. Such trends are typical for the solubility of gases in ionic liquids and DES [8]. Since the topic of utilizing DES for CO_2 capture is relatively new, few studies have been performed experimentally. One of the main experimental works that investigated CO_2 solubility in choline chloride/urea 1 : 2 was reported by Li et al. [9], Leron et al. [10], and Mirza et al. [8].

Li et al. [9] recently studied the solubility of CO_2 in DES systems formed with choline chloride and urea of three molar ratios (1 : 1.5, 1 : 2, and 1 : 2.5) at different temperatures and pressures up to 13 MPa. It was found that the solubility of CO_2 in choline chloride and urea DESs depends on three factors:

- (i) *The choline chloride to urea molar ratio*: the mixture composition ratio has a significant effect on the solubility of CO_2 (fixed pressure and temperature). It was found that the molar ratio of 1 choline chloride : 2 urea shows the highest CO_2 solubility compared with 1 : 1.5 and 1 : 2.5 molar ratios).
- (ii) *Pressure*: the solubility of CO_2 increases with pressure showing more sensitivity to low pressure range.
- (iii) *Temperature*: the solubility of CO_2 decreases with increasing temperature at all pressure values.

In addition, Leron et al. [10] studied CO_2 absorption in reline. In their work, approximately 200 mL of the degassed sample was loaded into the microbalance pan. The reactor vessel was closed, and the system was slowly purged with CO_2 for at least 1 h to remove other gases that may be present in the vessel. Then, the gas outlet valve of the reactor vessel was closed, and CO_2 gas was allowed to flow into the vessel until the desired pressure was reached. Then, the gas inlet valve was closed, the desired temperature was set, and the system was allowed to reach equilibrium when no change in weight was observed. The pressure was increased to the next desired value by introducing more gas into the system, and the equilibrium experiment was repeated up to 6.0 MPa and temperatures varied from 303.15 K to 343.15 K in 10 K intervals [10]. Figure 5 shows a comparison of CO_2 absorption data performed by Leron et al. and compared with similar work reported in the literature [10].

As Figure 5 shows, there is slight variation in the results between Li et al. [9] and Leron et al. [10] with the values reported by Leron et al. [10] being constantly lower than the values reported by Li et al. [9] for the solubility of CO_2 in reline. This variation might be related to the fact that Li et al. have reported their results in narrow range of temperatures and it might be as well related to the presence of preparation method, raw material sources, and presence of impurities in the prepared DES samples in both works.

Mirza et al. [8] experimentally studied the solubility of CO_2 in three DESs, namely, reline (choline chloride and urea in a 1 : 2 molar ratio), ethaline (choline chloride and ethylene glycol in a 1 : 2 molar ratio), and malinine (choline

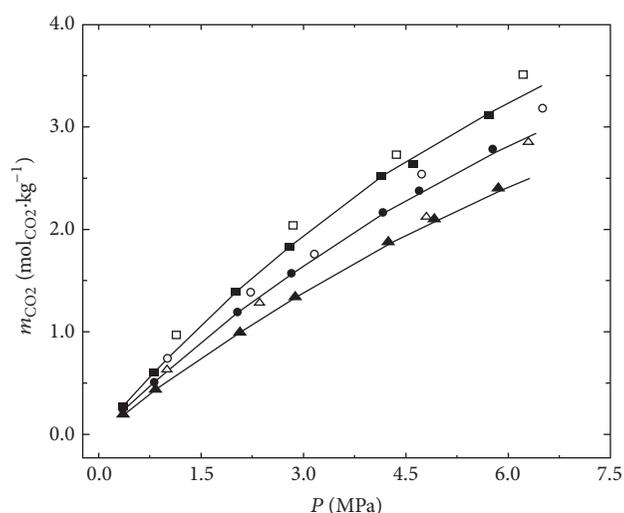


FIGURE 5: Comparison of experimental CO_2 solubility in 1 : 2 choline chloride-urea DES: (\square , 313.15 K; \circ , 323.15 K; \triangle , 333.15 K) Li et al. [9]; (\blacksquare , 313.15 K; \bullet , 323.15 K; \blacktriangle , 333.15 K) Leron et al. [10]; and lines, calculated by the extended Henry's law equation [10].

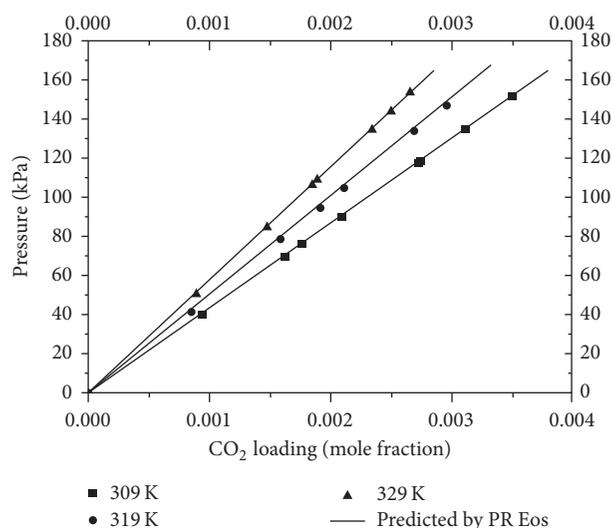


FIGURE 6: CO_2 solubility as a function of pressure in reline (choline chloride-urea 1 : 2) at 309 K (\blacksquare), 319 K (\bullet), and 329 K (\blacktriangle). Solid lines: predicted by Peng-Robinson Equation of State (PR EoS) [8].

chloride, malic acid, and ethylene glycol in a 1.3 : 1 : 2.2 molar ratio) in the temperature range of (309 to 329) K at pressures up to 160 kPa. They used thermodynamic modeling using a modified Peng–Robinson equation of state to correlate the experimental data (Figure 6).

Moreover, Mirza et al. have calculated Henry's constants for CO_2 –DES systems under the above-mentioned conditions giving values in the range of (3.7 to 6.1) MPa (on a molality basis) as shown in Figure 7.

Mirza et al. [8] calculated Gibbs free energy, enthalpy of dissolution, and entropy of dissolution (Table 2) which shows that the CO_2 absorption is exothermic and the entropy of the system falls as a result of gas absorption [8]. The negative

TABLE 2: Gibbs energy, enthalpy, and entropy for the CO₂-DES system at 0.1 MPa and 319 K as reported by Mirza et al. [8].

CO ₂ -DES system	$\Delta_{\text{dis}}G$ (kJ/mol)	$\Delta_{\text{dis}}H$ (kJ/mol)	$\Delta_{\text{dis}}S$ (kJ/mol·K)
CO ₂ -reline	16.46	-12.59	-91.04
CO ₂ -ethaline	16.38	-11.09	-86.07
CO ₂ -malinine	16.62	-12.65	-91.70

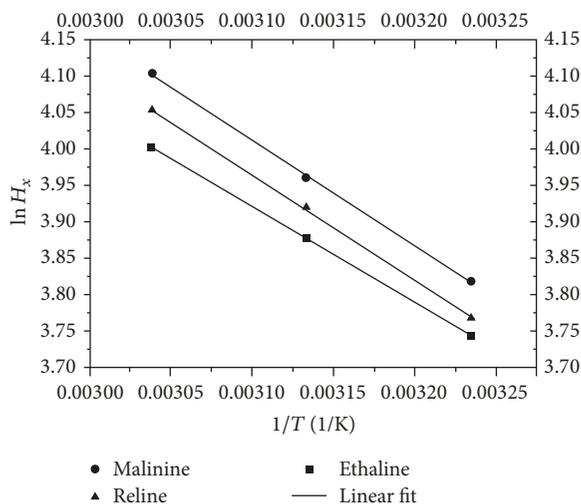


FIGURE 7: Variation of logarithm of Henry's constants (based upon mole fraction) for (■) ethaline (choline chloride and ethylene glycol in a 1:2 molar ratio), (▲) reline (choline chloride and urea in a 1:2 molar ratio), and (●) malinine (choline chloride, malic acid, and ethylene glycol in a 1.3:1:2.2 molar ratio with inverse of temperature [8].

values of $\Delta_{\text{dis}}H$ for all DESs indicate the presence of strong intermolecular bonding between the CO₂ and the DESs. It also shows that the process of dissolution is exothermic. Similarly, negative values for $\Delta_{\text{dis}}S$ show that a more ordered system is obtained after the dissolution of CO₂ in DESs. Larger negative values of $\Delta_{\text{dis}}S$ also imply that change in free energy would be positive for the CO₂ dissolution in DESs resulting in a nonspontaneous dissolution of gas in DESs [8].

5. Conclusion

This review summarizes the first prepared deep eutectic solvent "reline" that is made by mixing choline chloride and urea in 1:2 molar ratio due to the special properties of this DES as the one with the lowest melting point and high CO₂ absorption rate. Although the available experimental and theoretical studies are still scarce, this review is of special value to the researchers who look for comprehensive physiochemical properties of reline. Moreover, it summarizes the main factors that affect CO₂ solubility and the available CO₂ absorption data as reported up to date. The values show that this mixture is of great importance as a potential medium for an efficient CO₂ removal in natural gas and flue gas separation processes replacing the current amine-based absorption technology.

Conflicts of Interest

The authors declare no competing financial interests.

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