Deep Eutectic Solvents – ideal solution for clean air or hidden danger?

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Abstract: The industrial sector is one of the fastest-growing sources of greenhouse gases, due to its excessive energy consumption to meet the rapidly growing demand for energy-intensive products. The use of deep eutectic solvents (DESs) has been studied extensively in order to cope with these harmful gases, but their usage can be an issue in respect to ecological reasons. Do deep eutectic solvents harm the atmosphere? Yes, these solvents can be harmful if their constituents (HBA and HBD) that are volatile and toxic in nature. A number of scientific reports preset their application without care on cross-contamination of treated media. Herein, we highlight the ecotoxicity behavior of DESs as treatment materials for three major toxic gas treatment methods, including carbon dioxide (CO_2) capture, biogas treatment and air purification. Special attention is given to the health consequences of HBDs due to their toxicity and emission outside of the treatment system into the environment. The physicochemical characteristics of DESs are evaluated and addressed in comparison to the benchmark solvents. Emission of DESs can be predicted based on simulation software like COSMO-RS or Molecular Dynamics (MD). Furthermore, we suggest some simple protocols to estimate this issue and thus make aware researchers to think about it when experimenting with DES for different applications.

Keywords: Carbon Capture; waste gases treatment; flue gases treatment; biogas purification; fuels combustion; absorption; ammonia; hydrogen sulfide; BTEX; VOC.

1. Introduction

Green chemistry is concerned with the use and production routes of chemicals that are eco-friendlier. It motivates scientists either to minimize the use of toxic chemicals or to use alternative media, reaction conditions, and sources of energy [1-3]. The use of eco-friendly solvents and safer chemicals is one of the 12 principles of green chemistry. Among the most challenging issues facing researchers today are environmental issues and the energy crisis. Using sustainable components as part of this efficiency improvement will also alleviate environmental issues [4]. Global population growth and improved quality of life have led to an increase in energy demand, which is primarily derived from fossil fuels. In comparison with other fossil fuels, natural gas has the least adverse environmental effects. As a result of technological advancements, it has become more economic to extract natural gas from substandard reservoirs. Sub-quality natural gas contains impurities, such as CO_2, that must be eliminated since they are corrosive and reduce heating value [5, 6]. The removal of CO_2, ammonia and hydrogen sulfide present in biogas is essential for sustainability, resulting in higher energy consumption of these processes. The traditional methods for CO_2 capture from flue gases have involved the use of aqueous amine solutions as chemical solvents for the absorption of CO_2. These solutions include 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA) and monoethanolamine (MEA) [7-12]. In addition to being cheap, fast reacting, selective, and absorbing, they have a number of other desirable properties [13]. However, they are toxic, partially degradable, produce corrosive byproducts, require a lot of energy, and are expensive to acquire, so they are not eco-friendly. As a result, in recent years, the use of ecologically friendly solvents has gained a high attention [14]. In this regard, Ionic liquids (ILs) are a type of green solvent that have been used in a wide range of chemical techniques and processes [15, 16]. The majority of ILs are time-consuming and costly to synthetize. Furthermore, most of ILs have revealed to be highly polluting leading to negative effects on various living beings [15-18]. As a consequence, there is a need to replace ILs with more eco-friendly solvents. Deep eutectic solvents (DESs) are now regarded as one of the most promising IL replacement options. Undoubtedly, various studies have demonstrated that DESs present several similarities to IL [19], but less expensive, easy to synthesize, and more environment benign than IL [14, 20, 21]. However, some concerns are already raised regarding their potential toxicity [22]. A typical DES is made by combining low-cost components (with hydrogen-bond formation properties) to create a eutectic mixture with a melting point much lower than either of its individual components [19, 20, 23, 24]. Mostly, DES is made by combining a salt with a hydrogen-bond donor (HBD) molecule in various molar ratios [19]. Absorption plays a significant role in the core mechanism of operation of DES-based technologies for gas processing. The ability of deep eutectic solvents (DESs) to absorb toxic gases has significant potential [25]. DESs contain two or more constituents linked together through hydrogen bonds between the hydrogen-bond acceptor (HBA) and the hydrogen-bondg donor (HBD), π - π interaction or halogen bonds [26-28]. As an example, choline chloride (ChCl)/urea mixture, with a melting point value of 12 °C (in a 1:2 molar ratio), is in liquid state at room temperature, in which its melting point is much lower than the melting points of its constituents, e.g., the melting points of ChCl and urea are 302 and 133 °C, respectively [14, 19]. As for their applications, DESs have been proposed in several approaches including stationary phases for chromatography [29], absorption [30], analytical chemistry [31, 32], extraction [33-36], synthesis of materials [37-40], electrochemistry [19, 41, 42], drug discovery [43-45], lubrication [46], biotransformation [47], nanotechnology [48], among others. Natural deep eutectic solvents (NADES) are those that obtain DESs from natural sources, such as amino acids, sugars, urea, and organic acids [49]. However, risk evaluations for all current and prospective chemicals are a top priority for the European Union's REACH (Registration, Evaluation, and Authorization of Chemicals) regulation, as well as other global organizations [50]. According to characteristic of ideal solvent as given by EU's REACH regulation the solvent must have low toxicity, low volatility, low flammability but DESs meets all other parameters but only few drawbacks are more viscosity and toxic in nature. Therefore, it is very important to focus on the environment since the extensive use of DESs and their entrance into the industry could be a serious conservational problem, having a devastating impact on environments and, eventually on humankind. As a result, the impact of DESs on ecological systems should be investigated.

In general, DESs are often named as non-volatile, giving them the advantages of no loss and zero emission into the air. In contrast to the various papers on the stability of ionic liquids [40, 51], volatilization of DESs is rarely mentioned. However, such generalization about DESs, in many cases, can cause serious methodological issues in case of their studies or applications. In particular, DESs are studied as sorptive media for waste gases treatment. Several applications regarding CO_2 capture, treatment of hydrogen or biogas as well as air purification were recently published. Interestingly, some of these chemical compounds used for synthesis of DESs own a volatile or semi-volatile character. It is obvious that under dynamic conditions gas-liquid equilibrium will cause partial evaporation of these compounds. In most of the papers, this aspect of the study is omitted, thus published developments are out-off purpose for real scenario. This review timely highlights this aspect, summarizing the current state of the art in this field, as well as providing suggestions for future research in terms of good research practice.

2. Unaddressed concerns about DESs volatility in separation and purification of gaseous streams

2.1. CO_2 absorption

DESs have been explored in recent investigations for CO_2 capture due to their promising features, as shown in (Fig.1). We focused on HBDs that are generally organic and nonionic in nature, particularly those that are volatile and can cause serious health problems even at low concentrations. Many studies claim that DESs are environmentally friendly, but the issue remains unclear because their precursors often are volatile, and after use, they may evaporate in the surrounding environment, bringing serious respiratory problems as well as odorous nuisance. In addition, some of them can corrode technical equipment of the process installation and change their physical appearance. Phenol, for instance, is often used as HBD in DESs, which is known to be very corrosive to metals including Al, Cu and Al-Cu alloys [52].

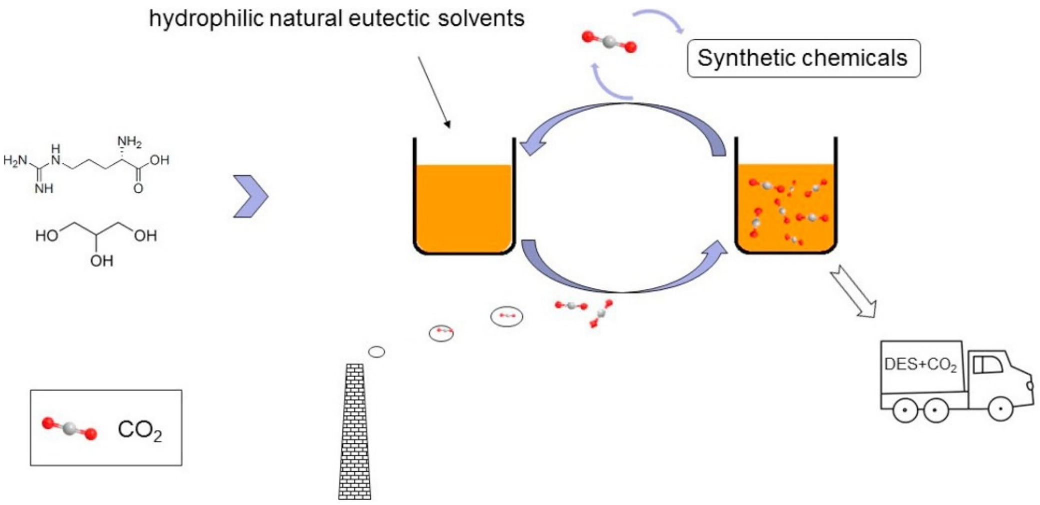

Fig. 1. DES with hydrophilic and natural bases for green CO_2 capture. "Reprinted from [53] Copyright (2018), with permission from Elsevier."

Phenol is easily absorbed into human body through a number of pathways (inhalation, skin contact and ingestion) and quickly spreads throughout the organism. The vapors of phenol are corrosive and toxic to the eyes, skin, and respiratory tract and it is also extremely toxic to neurons, if introduced to the bloodstream, it can cause immediate death by disrupting the neural transmission system.

We consider a few studies that used phenol as HBD. As DESs are formed by weak interactions (hydrogen bonds), it maintains the toxicity even after formation of DESs. Wang et al. reported two DESs tetrabutylphosphonium bromide - Phenol (TBPB-PhOH) (1:4) and tetrabutylphosphonium bromide - diethylene glycol (TBPB-DEG) (1:4), which revealed an outstanding result for CO_2 absorption [54]. Unfortunately, their HBD components are volatile in nature. Diethylene glycol is a low volatile organic compound that can cause liver damage, respiratory failure, and seizures. Li et al. synthesized ChCl/ mono ethanolamine (MEA) based DESs with good CO_2 absorption and reusability [55], although the HBD is relatively volatile and a corrosive chemical that can cause respiratory issues. Shukla et al. developed 1-methylimidazolium chloride and ethylene diamine (HmimCl: EDA) with a molar ratio (1:2) [56], which contains the HBD component EDA that irritates the nose and throat. Organic amines are known as odorous compounds, thus their emission at even very low rates will cause issues with air quality around the emitting facility. According to Liu et al., acetylcholine chloride and guaiacol (ACC/guaiacol) with a molar ratio (1:3) [57], their HBD part guaiacol, can induce respiratory tract irritation, skin irritation, and eye discomfort. Table (1) summarizes the toxicity of these HBDs. None of these studies addressed the aspect of DES components' volatility or loss of the DES during the operation.

Table 1. Compilation of the toxicity of precursors of DESs used for CO_2 Absorption.

Type of DESs	M.P (°C)	Mole Ratio	T (K) of treatment process	Ref (Application)	Problematic compound	Volatility	Toxicity	Ref (Toxicity)
TBPB:PhOH	HBA= 104 °C HBD=40.5 °C DES= not reported	1:4	343.15 K	[54]	Phenol	Volatile (b.p = 181.7 °C)	Irritation to the skin, eyes, nose, throat, Neurotoxin	[58]
TBPB:DEG	HBA=104 °C HBD=-6.5°C DES= not reported	1:4	343.15 K		Diethylene glycol	Low volatile (b.p = 244 °C)	Liver toxicity, respiratory failure, and seizures.	[59]
ChCl:MEA	HBA=302 °C HBD=10.3 °C DES= 4.54 °C	1:5	343.15	[55]	Mono ethanolamine	Volatile (b.p =170 °C)	Corrosive chemical, breathing problems	[60]
HmimCl:EDA	HBA= RTIL* HBD=8°C DES= not reported	1:2	353.15	[56]	Ethylene diamine	Volatile (bp= 116 °C)	Irritate the nose and throat	[61]
ACC:guaiacol	HBA=146-150 °C HBD=26–29 °C DES= not	1:3	353	[57]	Guaiacol	Volatile (b.p = 205 °C)	Causes respiratory tract irritation, Skin irritation, Eyes irritation.	[62]

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2.2.Biogas treatment

Biogas is produced under anaerobic conditions using specified bacteria and waste materials as feedstock, such as wastewater treatment sludge or dumpsites, as represented in (Fig.2). Biogas, which is composed of carbon dioxide (25–50%) and methane (50–75%) and other toxic substances, such as ammonia, hydrogen sulfide, linear hydrocarbons (HC), aromatic hydrocarbons (benzene, ethylbenzene, toluene, and xylenes (BTEX), halogen compounds, and siloxanes, must be removed from biogas before it can be converted into energy [63-65]. Besides, to remove these toxic contaminants from the biogas, scientists are experimenting with a variety of strategies, including absorption, adsorption, membrane technologies, cooling, and processes utilizing various types of catalysts [66-68].

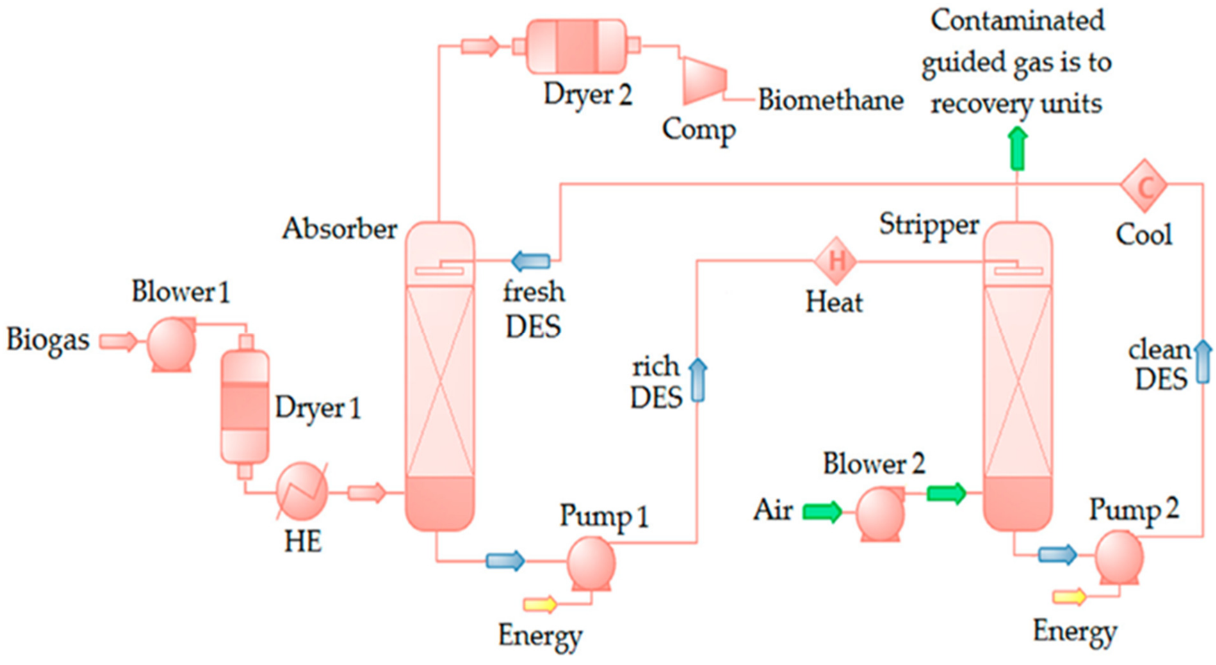

Fig.2. Scheme for the biogas upgrading technology [69, 70].

Here, we report few studies that have used DESs for biogas treatment, but their precursor, mainly HBD, have serious environmental issues. For example, Słupek et al. reported ChCl DEG based DESs for purification of biogas from toluene in which they used diethylene glycol (as HBD) [71]. This latter compound has low volatility, but is recognized to cause liver toxicity, respiratory failure, and seizures. In a more recent study, Słupek et al. reported [72] several DESs for theoretical and economic evaluation of low-cost DES for effective biogas upgrading to bio-methane. Selected DESs were formed using HBD volatile compounds, such as Butyric Acid, Ethylene glycol, Phenol, Methacrylic acid. All of these chemicals cause serious health issues especially breathing problems. Particularly, Butyric Acid has corrosive nature but also causes skin, nose, eyes, and lungs irritation. Ethylene glycol, for instance, causes irritation of mucous membranes and the upper respiratory tract, while Methacrylic acid is a highly corrosive chemical and contact with it can severely irritate and burn the skin and eyes with possible eye damage, nose irritation, coughing, and shortness of breath. The volatility of these HBDs is significant, as their boiling point values are: Methacrylic acid (b.p = 161 °C) > Butyric Acid (b.p = 163.5 °C) > Phenol (b.p = 181.7 °C) > Ethylene glycol (b.p = 197 °C) > diethylene glycol (b.p = 244 °C). A compilation of volatility and toxicity of these HBDs is given in Table (2).

Table 2. Comparison of toxicity of DESs precursors used for Biogas treatment.

Type of DESs	**M.P (°C)**	**Mole Ratio**	**T (K) of treatment process**	**Ref (Application)**	**Problematic compound**	**Volatility**	**Toxicity**	**Ref (Toxicity)**
Cl:DEG	HBA=302 °C HBD= 6.5°C DES= 17.8	1:2	353.15	[71]	diethylene glycol	Low volatile (b.p = 244 °C)	Liver toxicity, respiratory failure, and seizures.	[59]

	°C								
TEABr:Bu	HBA=286 °C HBD= −5.1 °C DES= not reported	(1:2)	293.15	[72]	Butyric Acid	Volatile (b.p = 163.5 °C)	Corrosive, Skin irritation, irritate Nose, Eyes, lungs	[73]
TBACl:EG	HBA= 41-44 °C HBD= -12.9 °C DES= not reported	1:3	293.15		Ethylene glycol	Volatile (b.p = 197 °C)	Irritation of mucous membranes and the upper respiratory tract.	[74]
TBABr:Ph	HBA=286 °C HBD=40.5 °C DES=not reported	1:2	293.15		Phenol	Volatile (b.p= 181.7 °C)	irritation to the skin, eyes, nose, throat, Neuro-toxin	[58]
ChCl:MthA	HBA=302 °C HBD= 14 to 15 °C DES= not reported	(1:2)	293.15		Methacrylic acid	Volatile (b.p = 161 °C)	Highly corrosive chemical and contact can severely irritate and burn the skin and eyes with possible eye damage. Nose irritation, coughing, shortness, of breath	[75]

According to figure 2, the recovery of absorbent takes place via stripping operation. To minimize the DES emission at the stripping stage it must be operated, at the lowest possible temperature and proper overpressure. Such solutions are known from different processes. For example, it is possible to separately strip-out ammonia and hydrogen sulfide from sour wastewater (according to Chevron WWT process) [76]. Same trapped impurities of biogas could be selectively stripped-out from DES. This aspect demands proper studies and modelling in future papers.

2.3 Air treatment

There are a number of toxic gases in waste air streams, including CO_2, SO_2, NO_X, H_2S, and Ammonia (NH_3), as shown in (Fig.3). Due to their harmful effects on the environment and human health, many countries restrict the release of certain gases into the atmosphere. Mitigation of greenhouse gas emissions is a major global challenge, considering their significant role in driving global warming and climate change.

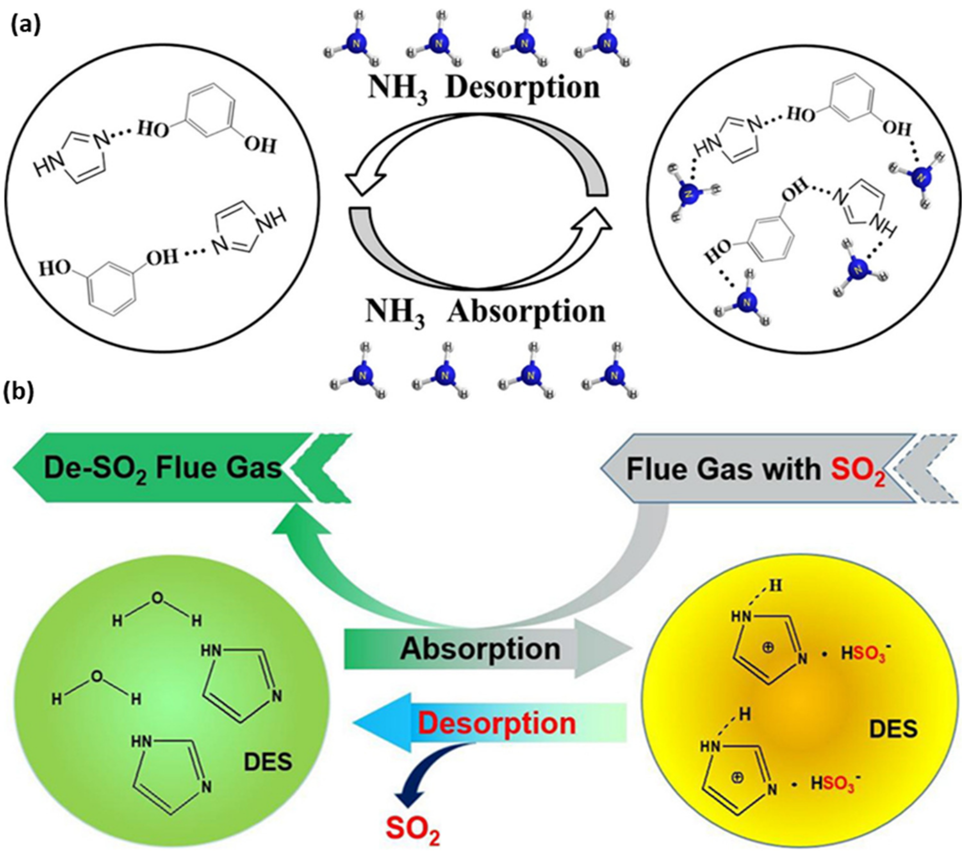

Fig.3. (a) DESs used for removal of NH_3."Reprinted from [77] Copyright (2021), with permission from Elsevier." (b) DESs used for removal of SO_2 “Adapted with permission form *[78]*. Copyright (2020) American Chemical Society”.

To some extent, the commercial processes for capturing these gases have a number of drawbacks, including the use of volatile solvents, the generation of hazardous byproducts, and a high energy expenditure [79]. Scrubbing with water or acids (mostly sulphuric acid, phosphoric acid, and organic acids) is widely used in numerous areas, but it has faced significant difficulties [80-82]. Due to the high vapour pressure and strong interaction between acid and NH_3, the absorbent recycling process consumes an enormous amount of energy. Additionally, it is challenging to avoid equipment corrosion while significant wastewater is generated during the method [77]. Over the last few decades, limestone has been used to control the emission of SO_2

[83]; unfortunately, large amounts of waste $CaSO_4$ and wastewater are generated during the process, and this waste prevents usable SO_2 from being recovered [84].

Presently, the use of DESs for the capture of toxic gases has received a lot of attention. Here, we report several studies that used DESs as a "green" approach for air treatment but their precursor, such as phenol, Resorcinol, Glycerol, Ethyl alcohol and Malonic acid, display serious health issues due to their volatile nature. Jiang et al. reported the application of ethylamine hydrochloride EaCl/phenol with a molar ratio (1:2) for NH_3 capture [85]. Luo et al. synthesized Imidazole (Im)/resorcinol (Res) Im/Res based DESs (1:1) for capture of NH_3 [77]. Resorcinol, used as HBD, is a semi-volatile compound with an aromatic odour and a sweetish bitter taste, so it is clear it will be emitted into the treated air, causing its pollution. According to the New Jersey Department of Health, breathing resorcinol can result in irritation to the throat and lungs, as well as cause drowsiness, tiredness, headache, and a blue colour to the skin and lips, a condition known as methemoglobinemia. It is known that exposure on resorcinol at very high levels can cause troubles with breathing, collapse and even death [86] (Table 3).

Table 3. Comparison of toxicity of DES components used for Air treatment.

Type of DESs	**M.P (°C)**	**Mole Ratio**	**T (K) of treatment process**	**Ref (Application)**	**Problematic compound**	**Volatility**	**Toxicity**	**Ref (Toxicity)**
EaCl:phenol	HBA=110.0 to 115.0 °C HBD=40.5 °C DES= not reported	1:2	293.2	[85]	Phenol	Volatile (b.p = 181.7 °C)	irritation to the skin, eyes, nose, throat, Neurotoxin	[58]
Im:Res	HBA=89 to 91 °C HBD= 110 °C DES= not reported	1:1	353.15	[77]	Resorcinol	Semi Volatile (b.p = 277°C)	Exposure to very high levels can cause trouble breathing, collapse and even death	[86]
ChCl:glycerol	HBA=302 °C HBD= 17.8 °C DES= 17.8 °C	1: 1	343.15	[25]	Glycerol	Semi-volatile (b.p =290 °C)	May cause irritation to skin, eyes, and respiratory tract and affects kidney	[87]
BA:P4444Cl	HBA= HBD= 122 °C DES= not reported	1:2	303.15	[88]	Benzoic acid	Semi-volatile (b.p = 249.2 °C)	eye damage, irritation of throat, nose, skin, coughing, and shortness of breath	[89]

ChCl:MA	HBA=302 °C HBD= 135 to 137 °C DES= −50 °C	1:1	343	[90]	Malonic acid	volatile (b.p = 140°C)	Corrosive, Irritant	[91]

Yang et al. synthetized ChCl–glycerol (1:1) DESs which showed excellent efficiency for SO_2 absorption *[25]*, but their HBD precursor glycerol is semi-volatile according to U.S. EPA Reference Method 24 (M24), which calculates volatility by converting weight percent loss at the end of 60 min at 110 °C in a forced draft oven into VOC content [92]. It may cause irritation to skin, eyes, and respiratory tract and affects kidney. Zhang Lvhong et al. synthesized tetra butyl phosphine chloride (P4444Cl) benzoic acid (BA) BA/P4444Cl based DESs with a molar ratio (1:2), which can reversibly and efficiently absorb nitric oxide (NO) [88], but their HBD part is benzoic acid which is semi volatile in nature. Health effects that can occur immediately or shortly after benzoic acid exposure include eye damage, irritation of throat, nose, skin, coughing, and shortness of breath. Sun et al. prepared ChCl:MA (Malonic acid) (1:1) DESs for SO_2 absorption [90] but its precursor Malonic acid owns serious environmental concerns such as corrosive, and irritant in nature.

The thermophysical properties of these toxic HBDs are very important to evaluate their harmful effects in environments. For instance, the n-octanol-water partition coefficient, often known as log P, is a measure of the distribution between hydrophobic and hydrophilic environments. It is calculated by taking the ratio of a chemical's solubility in n-octanol and its solubility in water. A higher Log P value indicates that the chemical is more hydrophobic (has a greater affinity for the octanol phase), whereas a lower Log P value suggests that the chemical is more hydrophilic (has a higher affinity for the water phase). The density (ρ) of a solvent is another significant parameter. On the other hand, the significance of this parameter is relatively minor in the absorption process. DES density values can influence the process of DES regeneration. Deep eutectic solvents, whose densities range greatly from common solvents, such as water, can be regenerated through extraction [93]. In table 4 detailed characteristics of these toxic HBDs are mentioned.

Table 4. Thermophysical properties of HBDs.

Compound	Log P (partition coefficient between n-octanol and water)	CAS number	Density	flash point	limit of exposition
Phenol	2.3	108-95-2	1.07 g/cm^3 at 20°C	79°C (174°F)	0.5 ppm an 8-hour TWA
Malonic acid	-1.45	141-82-2	1.6 g/cm^3 at 10°C - 25°C	171°C (340°F)	0.1 mg/m3 as an 8-hour TWA.
Mono ethanolamine	-1.45	111-42-2	1.02 g/cm^3 at 20 °C	85°C (185 °F).	0.1 mg/m3 as an 8-hour TWA
Ethylene diamine	0.45	105-57-7	0.945 g/cm^3 at 20 °C	34°C (93.2 °F)	0.5 ppm as an 8-hour TWA

Guaiacol	2.7	124-80-9	1.09 g/cm^3 at 20 °C	82°C (179°F)	0.1 mg/m3 as an 8-hour TWA
Ethylene glycol	-1.45	111-46-6	1.11 g/cm^3 at 20 °C	124°C (255.2°F)	5 mg/m3 as an 8-hour TWA.
Butyric Acid	-1.25	107-92-6	1.037 g/cm^3 at 25°C	72°C (161.6 °F)	0.5 ppm over an 8-hour TWA
Ethylene glycol	-1.45	107-21-1	1.09 g/cm^3 at 25°C	111-121°C (231.8-249.8 °F)	25 ppm over an 8-hour TWA
Methacrylic acid	-1.45	108-46-3	1.09 g/cm^3 at 25°C	170°F (77°C)	25 ppm as an 8-hour (TWA)
Resorcinol	2.3	108-46-3	1.27 g/cm^3 at 20°C	260.6 °F (127°C)	0.1 mg/m3 as an 8-hour

					TWA
Glycerol	-1.7	56-81-5	1.261 g/cm^3 at 25°C	350 °F (177 °C).	TLV of 5 mg/m3 for glycerol vapor.
benzoic acid	2.9	65-85-0	1.32 g/cm^3 at 20 °C	249.8 °F (121°C)	5 mg/m3 as 8-hour TWA

*ppm (parts per million), *TWA (time-weighted average), *TLV (Threshold Limit Value)

Flash point means the minimum temperature at which volatile combustible vapors ignite in air when exposed to a flame. According to the (table 4) the flash point values of these HBDs are higher than n-hexane (-22°C or -9°F) and aromatic solvents such as benzene, toluene, and xylene flash point values (< -17.78°C or < 0°F), (4°C or 39.2°F) and (32°C or 89.6°F) respectively. The limit of exposition, also known as the permissible exposure limit (PEL), is a legislative limit on the permissible air concentration of a substance. According to the Occupational Safety and Health Administration (OSHA), the permissible limit of hexane is 500 ppm averaged over an 8-hour work shift [94], Benzene has a limit of 1 ppm averaged over an 8-hour work shift and a maximum of 5 ppm during any 15-minute work period [95], Toluene has an average concentration of 200 ppm over an 8-hour work shift; 300 ppm cannot be exceeded during any 15-minute period. [96], and xylene has 100 ppm averaged over an 8-hour work shift

[97]. So, these benchmark solvents have much higher exposure limits as compared to HBDs but still they case a lot of problem. Thus, high awareness should be dedicated to processes based on DESs based on volatile HBD components.

n-Hexane is a highly toxic solvent that can cause nausea, headaches, vomiting, and dizziness. It can cause coma and death at greater concentrations. Also it irritates the skin and eyes [94]. In comparison, aromatic solvents such as benzene, toluene, and xylene are likewise extremely hazardous, with acute inhalation exposure causing depression of the central nervous system, nausea, vomiting, and dizziness. In addition, they influence the respiratory, central and peripheral nervous, gastrointestinal, cardiovascular, renal, hepatic, cutaneous, and hematological systems [95-97]. Deep eutectic solvents (DESs) are potentially competitive substitutes for benchmark solvents (such as n-hexane, aromatic, etc.) due to lower toxicity of some possible components. In order to assist in the implementation of the European strategy for a non-hazardous environment. There are several alternatives to n-hexane, aromatics and DES for the extraction of natural products, including solvent-free extraction, water, NADESs, bio-based solvents, supercritical fluids or liquefied gases.

Minimization of DES emission into the environment, beside selection of proper DES, could be obtained by “at the end of the pipe (absorber)” solutions such as trapping of DES vapors on adsorbent (like activated carbon), absorption in proper solvent (in case of hydrophilic compounds water could be used) or thermal/catalytic incineration. Compounds that are highly volatile, or evaporate more than 95% by weight in ambient conditions after 6 months (by definition named VOCs), are completely available to form ozone at rates proportional to their individual reactivity rates. The most challenging category of compounds to categorize is the semi-volatile category, which includes substances that evaporate between 5% and 95% by weight in 6 months when exposed to room temperature and relative humidity [92].

3. Outlook and Future Challenges

DESs are an interesting class of alternative solvents due to their advantages in terms of simplicity in synthesis and inexpensive, and they can be tailored to meet the needs of a specific method. These characteristics make DESs an ideal replacement for both ILs and typical organic solvents. This opens up exciting new possibilities for the development of truly eco-friendly solvent systems that meet the criteria for sustainable and green chemistry. DESs as solvents have versatile uses, such as catalysts, lubricants, additives, metal processing materials, synthetic materials, and energy materials, while considered environmentally friendly, benign, and non-toxic compounds. In this review, relevant findings revealed that their eco-friendly character is not entirely true and that such broad presumptions should be overlooked. Therefore, it is necessary to investigate ecotoxicological aspects due to their volatile and toxic precursors. We highlighted the toxicity and volatility of compounds used for DES synthesis and subsequently used for carbon capture, biogas treatment, and air treatment.

Risk assessment regarding the emission of DES components can be easily done under laboratory conditions. Here, we suggest some examples of protocols useful to control these issues – they relate to control of weight loss of DES, condensation as well as headspace-gas chromatography technique.

3.1. Weight loss of DESs

Weight loss of DESs is the key parameter for evaluation of their evaporation when applied as sorptive medium for gases treatment. Simple control of DES mass before and after the treatment process should allow for estimating the loss. However, in this case, it should be considered that the absorbed pollutant will increase the mass of the absorbent. This latter aspect can be adjusted based on the mass balance of the absorption process.

3.2. Condensation

In the case of gases treatment focused on the removal of low molecular impurities, such as hydrogen sulfide or CO_2 absorption, outlet gas could be subjected to a low-temperature condensation zone, where volatilized DES components could be effectively trapped and quantified.

3.4. Headspace technique coupled with gas chromatography

Headspace analysis, both under static or dynamic conditions, would be used to monitor the volatility of the DES components. In the first option, a specific amount of DES would be equilibrated in elevated conditions in a hermetic vial. Herein, a small portion of gas-phase (typically between 0.2-05 mL) would be sampled and analyzed by gas chromatography (GC) to inspect the concentration of the DES components in the gas phase. In the second option, volatile components emitted from DES would be continuously trapped on the solid sorbent, followed by thermal desorption of analytes into the GC. This protocol was already proved to be effective to detect phenol (a one of popular HBDs used for DES formation) in water matrix, which exhibits same interactions with phenol (hydrogen bonding) as most of HBAs [98]. Typically, a flame ionization detector or mass spectrometer would be used. However, in the case of DES components, more selective and sensitive detectors, such as electron capture detector (ECD, for halogen-containing compounds), flame photometric detector (FPD, for sulfur of phosphorous compounds) as well as nitrogen – phosphorous detector (NPD) would be used. Headspace analysis coupled with GC was used in several applications to evaluate the emission from many types of samples [98-103]. Such dedicated studies focused on the emission of DES components seem to be a good idea in near future. It is clear that high demand on such protocols and reports in relation to DESs currently exists.

3.4 Prediction of DES volatility by software

Deep eutectic solvents (DESs) are increasingly used in many industries due to their unique properties, such as volatility, viscosity and enhanced solubility. The prediction of their volatility is essential for many chemical processes, such as distillation and evaporation. To predict the volatility of DESs, several software programs and computer simulations have been developed. These programs and simulations use different methods to calculate the vapor pressure of the DES, and the accuracy of the results vary depending on the method used. With further research and development, these methods may become more accurate and reliable. These programs use mathematical equations to calculate the vapor pressure of a given DES. COSMO-RS is the one of the best softwares to predict the volatility of deep eutectic solvents by calculating their vapor pressure.

3.4.1 COSMO-RS

COSMO-RS is a powerful computational method that can be used to predict the volatility of deep eutectic solvents. It utilizes an advanced thermodynamic model to create a reliable prediction of the activity coefficients of the different components in the solution. It then combines this data with experimentally determined vapor pressures to accurately predict the vapor pressures of the solution. The resulting vapor pressures can then be used to predict the volatility of the DES. One of the primary goals of COSMO-RS is to determine the structure-property relationship of the DES structure [104-106].

COSMO-RS is a highly accurate and cost-effective method for predicting the volatility of DESs. It is capable of producing results that are comparable to experimental measurements and can save time, money, and materials when compared to traditional laboratory testing.

3.4.2 Simulating DESs

Another approach to predicting the volatility of DESs is to use computer simulations. Molecular dynamics (MD) simulates the motion of certain groupings of elements by solving the classical equations of motion, providing information on the atomic-scale system dynamics

[107]. It is used for validating the best-performing force field by obtaining agreement between simulated densities, volume expansion coefficients, heat capacities, and diffusion coefficients and actual results [108]. In this approach, the molecular structure of the DES is simulated using equations of motion to determine the behavior of the DES over time. This can be used to calculate the vapor pressure of the DES.

In another work, molecular simulations on multiple DESs revealed very high agreement with experimental densities and thermodynamic parameters. Anion-HBD interactions were found to be crucial for all four systems by structural and hydrogen bond studies [109].

4. Conclusions

Due to the nature and diversity of DESs, academic and industrial communities are gaining attention in these mixtures. It has been shown that DESs can be used for a wide range of purposes, including biocatalysts [110, 111], biotechnology [112, 113], food [114], pharmaceuticals [115, 116], or as a biofuel [117, 118]. Here, we focused on three major air treatment processes including carbon capture, biogas, and air treatment. We analyzed specific HBD compounds of DESs that can cause a serious health concerns in environments. Since such compounds need to be monitored over their use and further disposal, we also suggested some protocols to cope with these conditions and thus reduce their impact on the ecological systems.

It is clear, that in many studies the authors focused only on the removal effectiveness of target pollutants. The serious environmental risk related to the emission of DES components into the atmosphere is totally omitted. In our opinion, studies in this field without proper analysis and assurance of the DES zero-emission process shouldn’t be published, or at least make emphasis on the potential risk when manipulating such compounds. This is a clear example that science rather than offering new knowledge for promising solutions to society’s concerns affects potentially the existing ecosystems. At this point, we (researchers) must be aware when experimenting with the chemical synthesis of new feedstocks and their side effects in applications.

As a first step, to make a more green and clean solvent, a detailed database of the eco-and cytotoxicity aspects of DESs is required, including many outcomes and an appropriate combination of HBA/HBD. Secondly, it is necessary to develop computational predictive methods that consider the volatility of the components of the DES mixture as well as a variety of possible prediction scenarios [102]. Finally, the risk of emission should be quantitatively evaluated when performing experiments. Simple protocols to control DES emission based on headspace analysis coupled with gas chromatography were herein proposed. It is essential to consider the thermophysical parameters of DESs, such as their boiling point, vapor pressure, and flash point, when developing processes that use DESs. The physicochemical characteristics of DESs are discussed and evaluated in light of comparisons to conventional solvents.

Analysis of available literature reveals also additional concerns regarding the term "deep eutectic solvent", that is not taken seriously by most of researchers. Most of researchers use the DES term, regardless how big depletion of melting point comparing to pure components was observed. In our opinion, DES term should be reserved for mixtures having significant depletion of melting point, while for other mixtures a term “eutectic mixture” should be used [103]. In some cases, no report was available about the solid-liquid equilibrium of the mixtures discussed here. The authors didn’t study the melting point of formed DES, so it is impossible to even refer to them as "eutectic" solvents. In future papers, this aspect should be treated seriously, and researchers should measure the melting point of newly obtained DESs for their studies and on this basis refer to proper nomenclature of obtained mixtures.

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