

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

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21 **Abstract:** The industrial sector is one of the fastest-growing sources of greenhouse gases, due
22 to its excessive energy consumption to meet the rapidly growing demand for energy-intensive
23 products. The use of deep eutectic solvents (DESs) has been studied extensively in order to
24 cope with these harmful gases, but their usage can be an issue in respect to ecological reasons.
25 Do deep eutectic solvents harm the atmosphere? Yes, these solvents can be harmful if their
26 constituents (HBA and HBD) that are volatile and toxic in nature. A number of scientific re-
27 ports present their application without care on cross-contamination of treated media. Herein, we
28 highlight the ecotoxicity behavior of DESs as treatment materials for three major toxic gas
29 treatment methods, including carbon dioxide (CO₂) capture, biogas treatment and air purifica-
30 tion. Special attention is given to the health consequences of HBDs due to their toxicity and
31 emission outside of the treatment system into the environment. The physicochemical charac-
32 teristics of DESs are evaluated and addressed in comparison to the benchmark solvents.
33 Emission of DESs can be predicted based on simulation software like COSMO-RS or Molec-
34 ular Dynamics (MD). Furthermore, we suggest some simple protocols to estimate this issue and
35 thus make aware researchers to think about it when experimenting with DES for different
36 applications.

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



40 1. Introduction

41 Green chemistry is concerned with the use and production routes of chemicals that are
42 eco-friendlier. It motivates scientists either to minimize the use of toxic chemicals or to use
43 alternative media, reaction conditions, and sources of energy [1-3]. The use of eco-friendly
44 solvents and safer chemicals is one of the 12 principles of green chemistry. Among the most
45 challenging issues facing researchers today are environmental issues and the energy crisis.
46 Using sustainable components as part of this efficiency improvement will also alleviate envi-
47 ronmental issues [4]. Global population growth and improved quality of life have led to an
48 increase in energy demand, which is primarily derived from fossil fuels. In comparison with
49 other fossil fuels, natural gas has the least adverse environmental effects. As a result of tech-
50 nological advancements, it has become more economic to extract natural gas from substandard
51 reservoirs. Sub-quality natural gas contains impurities, such as CO₂, that must be eliminated
52 since they are corrosive and reduce heating value [5, 6]. The removal of CO₂, ammonia and
53 hydrogen sulfide present in biogas is essential for sustainability, resulting in higher energy
54 consumption of these processes. The traditional methods for CO₂ capture from flue gases have
55 involved the use of aqueous amine solutions as chemical solvents for the absorption of CO₂.
56 These solutions include 2-amino-2-methyl-1-propanol (AMP), methyldiethanolamine (MDEA)
57 and monoethanolamine (MEA) [7-12]. In addition to being cheap, fast reacting, selective, and
58 absorbing, they have a number of other desirable properties [13]. However, they are toxic,
59 partially degradable, produce corrosive byproducts, require a lot of energy, and are expensive to
60 acquire, so they are not eco-friendly. As a result, in recent years, the use of ecologically friendly
61 solvents has gained a high attention [14]. In this regard, Ionic liquids (ILs) are a type of green
62 solvent that have been used in a wide range of chemical techniques and processes [15, 16]. The
63 majority of ILs are time-consuming and costly to synthesize. Furthermore, most of ILs have
64 revealed to be highly polluting leading to negative effects on various living beings [15-18]. As a



65 consequence, there is a need to replace ILs with more eco-friendly solvents. Deep eutectic
66 solvents (DESs) are now regarded as one of the most promising IL replacement options. Un-
67 doubtedly, various studies have demonstrated that DESs present several similarities to IL [19],
68 but less expensive, easy to synthesize, and more environment benign than IL [14, 20, 21].
69 However, some concerns are already raised regarding their potential toxicity [22]. A typical
70 DES is made by combining low-cost components (with hydrogen-bond formation properties) to
71 create a eutectic mixture with a melting point much lower than either of its individual com-
72 ponents [19, 20, 23, 24]. Mostly, DES is made by combining a salt with a hydrogen-bond donor
73 (HBD) molecule in various molar ratios [19]. Absorption plays a significant role in the core
74 mechanism of operation of DES-based technologies for gas processing. The ability of deep
75 eutectic solvents (DESs) to absorb toxic gases has significant potential [25]. DESs contain two
76 or more constituents linked together through hydrogen bonds between the hydrogen-bond
77 acceptor (HBA) and the hydrogen-bond donor (HBD), π - π interaction or halogen bonds
78 [26-28]. As an example, choline chloride (ChCl)/urea mixture, with a melting point value of 12
79 °C (in a 1:2 molar ratio), is in liquid state at room temperature, in which its melting point is
80 much lower than the melting points of its constituents, e.g., the melting points of ChCl and urea
81 are 302 and 133 °C, respectively [14, 19]. As for their applications, DESs have been proposed
82 in several approaches including stationary phases for chromatography [29], absorption [30],
83 analytical chemistry [31, 32], extraction [33-36], synthesis of materials [37-40], electrochem-
84 istry [19, 41, 42], drug discovery [43-45], lubrication [46], biotransformation [47], nanotech-
85 nology [48], among others. Natural deep eutectic solvents (NADES) are those that obtain DESs
86 from natural sources, such as amino acids, sugars, urea, and organic acids [49]. However, risk
87 evaluations for all current and prospective chemicals are a top priority for the European Union's
88 REACH (Registration, Evaluation, and Authorization of Chemicals) regulation, as well as other
89 global organizations [50]. According to characteristic of ideal solvent as given by EU's REACH



90 regulation the solvent must have low toxicity, low volatility, low flammability but DESs meets
91 all other parameters but only few drawbacks are more viscosity and toxic in nature. Therefore,
92 it is very important to focus on the environment since the extensive use of DESs and their
93 entrance into the industry could be a serious conservational problem, having a devastating
94 impact on environments and, eventually on humankind. As a result, the impact of DESs on
95 ecological systems should be investigated.

96 In general, DESs are often named as non-volatile, giving them the advantages of no loss and
97 zero emission into the air. In contrast to the various papers on the stability of ionic liquids [40,
98 51], volatilization of DESs is rarely mentioned. However, such generalization about DESs, in
99 many cases, can cause serious methodological issues in case of their studies or applications. In
100 particular, DESs are studied as sorptive media for waste gases treatment. Several applications
101 regarding CO₂ capture, treatment of hydrogen or biogas as well as air purification were recently
102 published. Interestingly, some of these chemical compounds used for synthesis of DESs own a
103 volatile or semi-volatile character. It is obvious that under dynamic conditions gas-liquid
104 equilibrium will cause partial evaporation of these compounds. In most of the papers, this
105 aspect of the study is omitted, thus published developments are out-off purpose for real sce-
106 nario. This review timely highlights this aspect, summarizing the current state of the art in this
107 field, as well as providing suggestions for future research in terms of good research practice.

108 **2. Unaddressed concerns about DESs volatility in separation and purification of gaseous** 109 **streams**

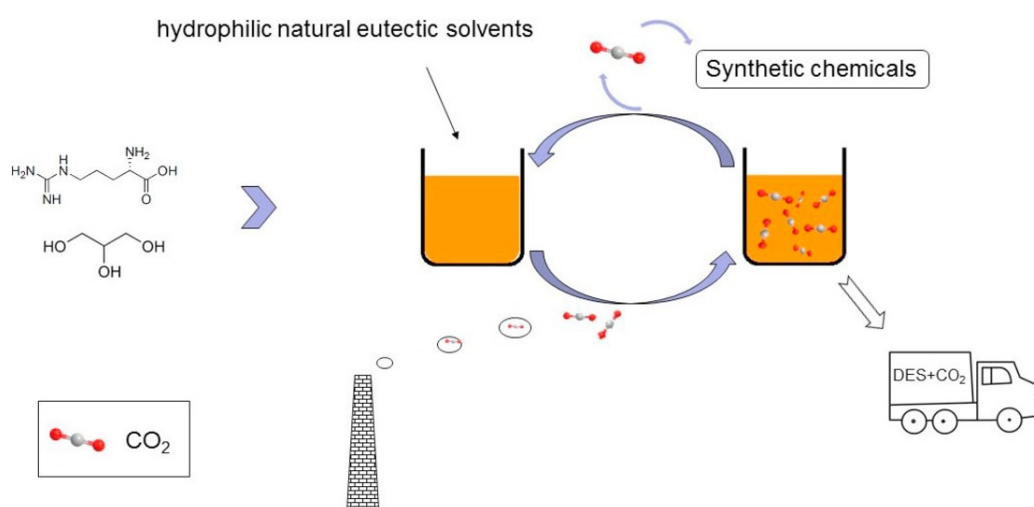
110 2.1. CO₂ absorption

111 DESs have been explored in recent investigations for CO₂ capture due to their promising fea-
112 tures, as shown in (Fig.1). We focused on HBDs that are generally organic and nonionic in
113 nature, particularly those that are volatile and can cause serious health problems even at low



114 concentrations. Many studies claim that DESs are environmentally friendly, but the issue re-
115 mains unclear because their precursors often are volatile, and after use, they may evaporate in
116 the surrounding environment, bringing serious respiratory problems as well as odorous nui-
117 sance. In addition, some of them can corrode technical equipment of the process installation and
118 change their physical appearance. Phenol, for instance, is often used as HBD in DESs, which is
119 known to be very corrosive to metals including Al, Cu and Al-Cu alloys [52].

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121

122 Fig. 1. DES with hydrophilic and natural bases for green CO₂ capture. "Reprinted from [53]

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

129 We consider a few studies that used phenol as HBD. As DESs are formed by weak interactions
130 (hydrogen bonds), it maintains the toxicity even after formation of DESs. Wang et al. reported
131 two DESs tetrabutylphosphonium bromide - Phenol (TBPB-PhOH) (1:4) and tetrabu-

132 tylphosphonium bromide - diethylene glycol (TBPB-DEG) (1:4), which revealed an out-
133 standing result for CO₂ absorption [54]. Unfortunately, their HBD components are volatile in
134 nature. Diethylene glycol is a low volatile organic compound that can cause liver damage,
135 respiratory failure, and seizures. Li et al. synthesized ChCl/ mono ethanolamine (MEA) based
136 DESs with good CO₂ absorption and reusability [55], although the HBD is relatively volatile
137 and a corrosive chemical that can cause respiratory issues. Shukla et al. developed
138 1-methylimidazolium chloride and ethylene diamine (HmimCl: EDA) with a molar ratio (1:2)
139 [56], which contains the HBD component EDA that irritates the nose and throat. Organic
140 amines are known as odorous compounds, thus their emission at even very low rates will cause
141 issues with air quality around the emitting facility. According to Liu et al., acetylcholine chlo-
142 ride and guaiacol (ACC/guaiacol) with a molar ratio (1:3) [57], their HBD part guaiacol, can
143 induce respiratory tract irritation, skin irritation, and eye discomfort. Table (1) summarizes the
144 toxicity of these HBDs. None of these studies addressed the aspect of DES components' vola-
145 tility or loss of the DES during the operation.

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Table 1. Compilation of the toxicity of precursors of DESs used for CO₂ Absorption.

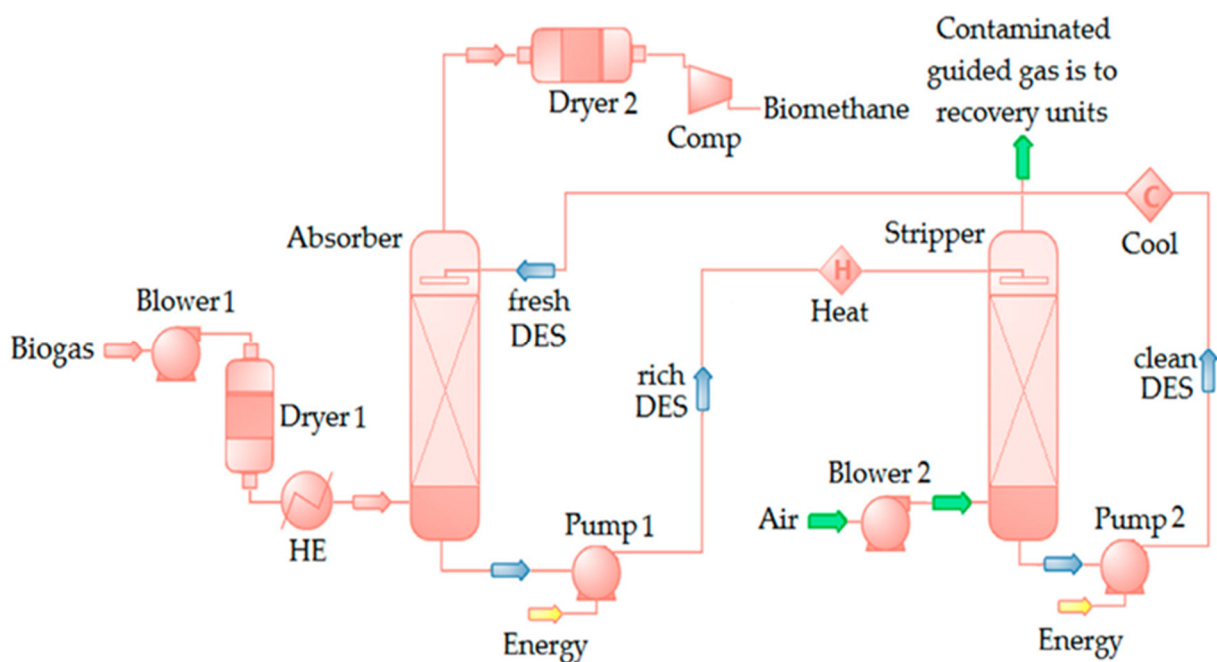
Type of DESs	M.P (°C)	Mole Ratio	T (K) of treatment process	Ref (Application)	Problematic compound	Volatility	Toxicity	Ref (Toxicity)
TBPB:PhOH	HBA= 104 °C HBD=40.5 °C DES= not reported	1:4	343.15 K	[54]	Phenol	Volatile (b.p = 181.7 °C)	Irritation to the skin, eyes, nose, throat, Neurotoxin	[58]
TBPB:DEG	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 ethanamine	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 reported	1:3	353	[57]	Guaiacol	Volatile (b.p = 205 °C)	Causes respiratory tract irritation, Skin irritation, Eyes irritation.	[62]

	reported							
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148 *RTIL – ROOM TEMPERATURE IONIC LIQUID

149 2.2. Biogas treatment

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



159
160 Fig.2. Scheme for the biogas upgrading technology [69, 70].

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

177 **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)
Ch: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		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 mu- cous membranes and the upper respiratory tract.	[74]
TBABr:Ph	HBA=286 °C HBD=40.5 °C DES=not reported	1:2	293.15	[72]	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 se- verely irritate and burn the skin and eyes with possi- ble eye damage. Nose irritation, coughing, short- ness, of breath	[75]

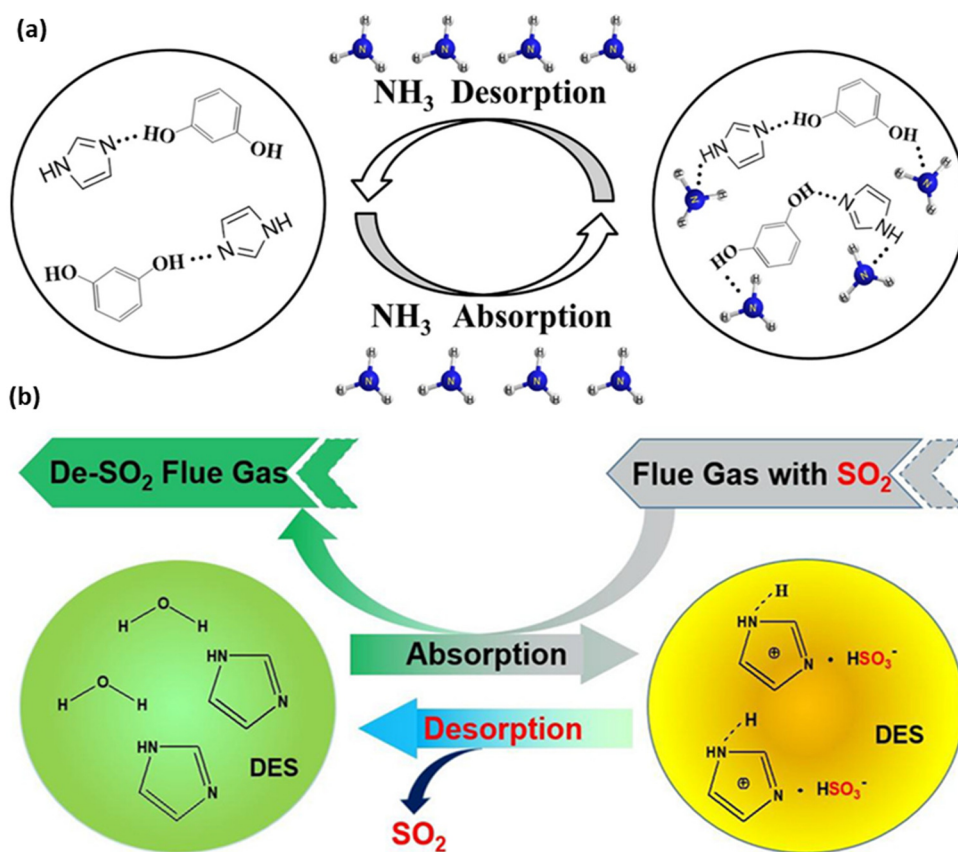


178 According to figure 2, the recovery of absorbent takes place via stripping operation. To mini-
179 mize the DES emission at the stripping stage it must be operated, at the lowest possible tem-
180 perature and proper overpressure. Such solutions are known from different processes. For
181 example,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

185 **2.3 Air treatment**

186 There are a number of toxic gases in waste air streams, including CO₂, SO₂, NO_x, H₂S, and
187 Ammonia (NH₃), as shown in (Fig.3). Due to their harmful effects on the environment and
188 human health, many countries restrict the release of certain gases into the atmosphere.
189 Mitigation of greenhouse gas emissions is a major global challenge, considering their
190 significant role in driving global warming and climate change.

191



192

193 Fig.3. (a) DESs used for removal of NH₃. "Reprinted from [77] Copyright (2021), with per-
 194 mission from Elsevier." (b) DESs used for removal of SO₂ "Adapted with permission from
 195 [78]. Copyright (2020) American Chemical Society".

196

197 To some extent, the commercial processes for capturing these gases have a number of draw-
 198 backs, including the use of volatile solvents, the generation of hazardous byproducts, and a high
 199 energy expenditure [79]. Scrubbing with water or acids (mostly sulphuric acid, phosphoric
 200 acid, and organic acids) is widely used in numerous areas, but it has faced significant difficul-
 201 ties [80-82]. Due to the high vapour pressure and strong interaction between acid and NH₃, the
 202 absorbent recycling process consumes an enormous amount of energy. Additionally, it is
 203 challenging to avoid equipment corrosion while significant wastewater is generated during the
 204 method [77]. Over the last few decades, limestone has been used to control the emission of SO₂

205 [83]; unfortunately, large amounts of waste CaSO_4 and wastewater are generated during the
206 process, and this waste prevents usable SO_2 from being recovered [84].

207 Presently, the use of DESs for the capture of toxic gases has received a lot of attention. Here, we
208 report several studies that used DESs as a “green” approach for air treatment but their precursor,
209 such as phenol, Resorcinol, Glycerol, Ethyl alcohol and Malonic acid, display serious health
210 issues due to their volatile nature. Jiang et al. reported the application of ethylamine hydro-
211 chloride $\text{Et}_3\text{N}/\text{phenol}$ with a molar ratio (1:2) for NH_3 capture [85]. Luo et al. synthesized
212 Imidazole (Im)/resorcinol (Res) Im/Res based DESs (1:1) for capture of NH_3 [77]. Resorcinol,
213 used as HBD, is a semi-volatile compound with an aromatic odour and a sweetish bitter taste, so
214 it is clear it will be emitted into the treated air, causing its pollution. According to the New
215 Jersey Department of Health, breathing resorcinol can result in irritation to the throat and lungs,
216 as well as cause drowsiness, tiredness, headache, and a blue colour to the skin and lips, a con-
217 dition known as methemoglobinemia. It is known that exposure on resorcinol at very high
218 levels can cause troubles with breathing, collapse and even death [86] (Table 3).

219

220



221 **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]
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223 Yang et al. synthesized ChCl–glycerol (1:1) DESs which showed excellent efficiency for SO₂
224 absorption [25], but their HBD precursor glycerol is semi-volatile according to U.S. EPA
225 Reference Method 24 (M24), which calculates volatility by converting weight percent loss at
226 the end of 60 min at 110 °C in a forced draft oven into VOC content [92]. It may cause irritation
227 to skin, eyes, and respiratory tract and affects kidney. Zhang Lvhong et al. synthesized tetra
228 butyl phosphine chloride (P4444Cl) benzoic acid (BA) BA/P4444Cl based DESs with a molar
229 ratio (1:2), which can reversibly and efficiently absorb nitric oxide (NO) [88], but their HBD
230 part is benzoic acid which is semi volatile in nature. Health effects that can occur immediately
231 or shortly after benzoic acid exposure include eye damage, irritation of throat, nose, skin,
232 coughing, and shortness of breath. Sun et al. prepared ChCl:MA (Malonic acid) (1:1) DESs for
233 SO₂ absorption [90] but its precursor Malonic acid owns serious environmental concerns such
234 as corrosive, and irritant in nature.

235 The thermophysical properties of these toxic HBDs are very important to evaluate their
236 harmful effects in environments. For instance, the n-octanol-water partition coefficient, often
237 known as log P, is a measure of the distribution between hydrophobic and hydrophilic envi-
238 ronments. It is calculated by taking the ratio of a chemical's solubility in n-octanol and its
239 solubility in water. A higher Log P value indicates that the chemical is more hydrophobic (has a
240 greater affinity for the octanol phase), whereas a lower Log P value suggests that the chemical
241 is more hydrophilic (has a higher affinity for the water phase). The density (ρ) of a solvent is
242 another significant parameter. On the other hand, the significance of this parameter is relatively
243 minor in the absorption process. DES density values can influence the process of DES regen-



244 eration. Deep eutectic solvents, whose densities range greatly from common solvents, such as
 245 water, can be regenerated through extraction [93]. In table 4 detailed characteristics of these
 246 toxic HBDs are mentioned.

247 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/m ³ as an 8-hour TWA.
Mono ethan-olamine	-1.45	111-42-2	1.02 g/cm ³ at 20 °C	85°C (185 °F).	0.1 mg/m ³ as an 8-hour TWA
Ethylene di-amine	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/m ³ 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/m ³ 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/m ³ 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/m ³ 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/m ³ as 8-hour TWA

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

249

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

261 [97]. So, these benchmark solvents have much higher exposure limits as compared to HBDs but
262 still they cause a lot of problem. Thus, high awareness should be dedicated to processes based on
263 DESs based on volatile HBD components.

264 n-Hexane is a highly toxic solvent that can cause nausea, headaches, vomiting, and dizziness.

265 It can cause coma and death at greater concentrations. Also it irritates the skin and eyes [94].

266 In comparison, aromatic solvents such as benzene, toluene, and xylene are likewise extremely

267 hazardous, with acute inhalation exposure causing depression of the central nervous system,

268 nausea, vomiting, and dizziness. In addition, they influence the respiratory, central and pe-

269 ripheral nervous, gastrointestinal, cardiovascular, renal, hepatic, cutaneous, and hematological

270 systems [95-97]. Deep eutectic solvents (DESs) are potentially competitive substitutes for

271 benchmark solvents (such as n-hexane, aromatic, etc.) due to lower toxicity of some possible

272 components. In order to assist in the implementation of the European strategy for a

273 non-hazardous environment. There are several alternatives to n-hexane, aromatics and DES

274 for the extraction of natural products, including solvent-free extraction, water, NADESs,

275 bio-based solvents, supercritical fluids or liquefied gases.

276 Minimization of DES emission into the environment, beside selection of proper DES, could be

277 obtained by “at the end of the pipe (absorber)” solutions such as trapping of DES vapors on

278 adsorbent (like activated carbon), absorption in proper solvent (in case of hydrophilic com-

279 pounds water could be used) or thermal/catalytic incineration. Compounds that are highly

280 volatile, or evaporate more than 95% by weight in ambient conditions after 6 months (by def-

281 inition named VOCs), are completely available to form ozone at rates proportional to their



282 individual reactivity rates. The most challenging category of compounds to categorize is the
283 semi-volatile category, which includes substances that evaporate between 5% and 95% by
284 weight in 6 months when exposed to room temperature and relative humidity [92].

285

286 **3. Outlook and Future Challenges**

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

299 Risk assessment regarding the emission of DES components can be easily done under labora-
300 tory conditions. Here, we suggest some examples of protocols useful to control these issues –
301 they relate to control of weight loss of DES, condensation as well as headspace-gas chroma-
302 tography technique.

303 *3.1. Weight loss of DESs*

304 Weight loss of DESs is the key parameter for evaluation of their evaporation when applied as
305 sorptive medium for gases treatment. Simple control of DES mass before and after the treat-
306 ment process should allow for estimating the loss. However, in this case, it should be consid-



307 ered that the absorbed pollutant will increase the mass of the absorbent. This latter aspect can be
308 adjusted based on the mass balance of the absorption process.

309 *3.2. Condensation*

310 In the case of gases treatment focused on the removal of low molecular impurities, such as
311 hydrogen sulfide or CO₂ absorption, outlet gas could be subjected to a low-temperature con-
312 densation zone, where volatilized DES components could be effectively trapped and quantified.

313 *3.4. Headspace technique coupled with gas chromatography*

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

331 *3.4 Prediction of DES volatility by software*



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

342 *3.4.1 COSMO-RS*

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

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

353 *3.4.2 Simulating DESs*

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



357 [107]. It is used for validating the best-performing force field by obtaining agreement between
358 simulated densities, volume expansion coefficients, heat capacities, and diffusion coefficients
359 and actual results [108]. In this approach, the molecular structure of the DES is simulated using
360 equations of motion to determine the behavior of the DES over time. This can be used to cal-
361 culate the vapor pressure of the DES.

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

365 **4. Conclusions**

366 Due to the nature and diversity of DESs, academic and industrial communities are gaining
367 attention in these mixtures. It has been shown that DESs can be used for a wide range of pur-
368 poses, including biocatalysts [110, 111], biotechnology [112, 113], food [114], pharmaceuticals
369 [115, 116], or as a biofuel [117, 118]. Here, we focused on three major air treatment processes
370 including carbon capture, biogas, and air treatment. We analyzed specific HBD compounds of
371 DESs that can cause a serious health concerns in environments. Since such compounds need to
372 be monitored over their use and further disposal, we also suggested some protocols to cope with
373 these conditions and thus reduce their impact on the ecological systems.

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



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

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

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405 **References**

406 [1] P.T. Anastas, Warner, J.C., Green Chemistry: Theory and Practice, in, 1998.

407 [2] M. Tobiszewski, A. Mechlińska, J. Namieśnik, Green analytical chemistry—theory and practice, *Chem. Soc. Rev.*,
408 39 (2010) 2869-2878. <https://doi.org/10.1039/B926439F>.

409

410 [3] L.H. Keith, L.U. Gron, J.L. Young, Green analytical methodologies, *Chem. Rev.*, 107 (2007)
411 2695-2708. <https://doi.org/10.1021/cr068359e>.

412

413 [4] R. Haghbakhsh, S. Raeissi, Deep eutectic solvents for CO₂ capture from natural gas by energy and exergy
414 analyses, *J. Environ. Chem. Eng.*, 7 (2019) 103411. <https://doi.org/10.1016/j.jece.2019.103411>.

415

416 [5] J. Haslback, N. Kuehn, E. Lewis, L.L. Pinkerton, J. Simpson, M.J. Turner, E. Varghese, M. Woods, Cost and
417 Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity,
418 Revision 2a, in, National Energy Technology Laboratory (NETL), Pittsburgh, PA, Morgantown, West Virginia,
419 2013.

420 [6] L. Zubeir, Carbon capture with novel low-volatile solvents: experiments and modeling, in: [Phd Thesis 1
421 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Universiteit Eindhoven.,
422 2016.

423 [7] K. Shunji, S. Xizhou, Y. Wenze, Investigation of CO₂ desorption kinetics in MDEA and MDEA+DEA rich
424 amine solutions with thermo-gravimetric analysis method, *Int. J. Greenh. Gas Control*, 95 (2020)
425 102947. <https://doi.org/10.1016/j.ijggc.2019.102947>.

426



427 [8] A.A. Nozaeim, A. Tavasoli, H.R. Mortaheb, M. Mafi, CO₂ absorption/desorption in aqueous DEEA/MDEA
428 and their hybrid solutions with sulfolane, *J. Nat. Gas Sci. Eng.*, 76(2020)
429 103219. <https://doi.org/10.1016/j.jngse.2020.103219>.

430

431 [9] E. Skylogianni, C. Perinu, B.Y. Cervantes Gameros, H.K. Knuutila, Carbon dioxide solubility in mixtures of
432 methyldiethanolamine with monoethylene glycol, monoethylene glycol–water, water and triethylene glycol, *J.*
433 *Chem. Thermodyn.*, 151 (2020) 106176. <https://doi.org/10.1016/j.jct.2020.106176>.

434

435 [10] D. Pandey, M.K. Mondal, Equilibrium CO₂ solubility in the aqueous mixture of MAE and AEEA:
436 Experimental study and development of modified thermodynamic model, *Fluid Ph. Equilibria.*, 522 (2020)
437 112766. <https://doi.org/10.1016/j.fluid.2020.112766>.

438

439 [11] F.K. Ayittey, A. Saptoru, P. Kumar, M.K. Wong, Energy-saving process configurations for
440 monoethanolamine-based CO₂ capture system, *Asia-Pac. J. Chem. Eng.*, 16(2021) e2576. <https://doi.org/10.1002/apj.2576>.

441

442 [12] A. Hartono, R. Ahmad, M. Usman, N. Asif, H.F. Svendsen, Solubility of CO₂ in 0.1M, 1M and 3M of
443 2-amino-2-methyl-1-propanol (AMP) from 313 to 393K and model representation using the eNRTL framework,
444 *Fluid Ph. Equilibria.*, 511 (2020) 112485. <https://doi.org/10.1016/j.fluid.2020.112485>.

445



446 [13] G. Li, D. Deng, Y. Chen, H. Shan, N. Ai, Solubilities and thermodynamic properties of CO₂ in
447 choline-chloridebaseddeep eutectic solvents, *J. Chem. Thermodyn.*, 75(2014)
448 58-62. <https://doi.org/10.1016/j.jct.2014.04.012>.

449
450 [14] B. Kudlak, K. Owczarek, J. Namieśnik, Selected issues related to the toxicity of ionic liquids and deep eutectic
451 solvents—a review, *Environ. Sci. Pollut. Res.*, 22 (2015) 11975-11992. <https://doi.org/10.1007/s11356-015-4794-y>.

452
453 [15] M.C. Bubalo, K. Radošević, I.R. Redovniković, J. Halambek, V.G. Srček, A brief overview of the potential
454 environmental hazards of ionic liquids, *Ecotoxicol. Environ. Saf.*, 99(2014)
455 1-12. <https://doi.org/10.1016/j.ecoenv.2013.10.019>.

456
457 [16] R.N. Das, K. Roy, Advances in QSPR/QSTR models of ionic liquids for the design of greener solvents of the
458 future, *Mol. Divers.*, 17 (2013) 151-196. <https://doi.org/10.1007/s11030-012-9413-y>.

459
460 [17] I. Juneidi, M. Hayyan, O. Mohd Ali, Toxicity profile of choline chloride-based deep eutectic solvents for fungi
461 and *Cyprinus carpio* fish, *Environ. Sci. Pollut. Res.*, 23 (2016) 7648-7659. <https://doi.org/10.1007/s11356-015-6003-4>.

462
463 [18] T.P.T. Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: a review, *Water Res.*, 44
464 (2010) 352-372. <https://doi.org/10.1016/j.watres.2009.09.030>.

465



466 [19] E.L. Smith, A.P. Abbott, K.S. Ryder, Deep eutectic solvents (DESs) and their applications, *Chem. Rev.*, 114
467 (2014) 11060-11082.<https://doi.org/10.1021/cr300162p>.

468

469 [20] A. Shishov, A. Bulatov, M. Locatelli, S. Carradori, V. Andruch, Application of deep eutectic solvents in
470 analytical chemistry. A review, *Microchem. J.*, 135 (2017) 33-38.<https://doi.org/10.1016/j.microc.2017.07.015>.

471

472 [21] J. Płotka-Wasyłka, M. Rutkowska, K. Owczarek, M. Tobiszewski, J. Namieśnik, Extraction with
473 environmentally friendly solvents, *TrAC-Trends Anal. Chem.*, 91(2017) 12-25.<https://doi.org/10.1016/j.trac.2017.03.006>.

474

475 [22] M. Marchel, H. Cieśliński, G. Boczkaj, Deep eutectic solvents microbial toxicity: Current state of art and
476 critical evaluation of testing methods, *J. Hazard. Mater.*, 425(2022) 127963.<https://doi.org/10.1016/j.jhazmat.2021.127963>.

477

478 [23] D. Carriazo, M.C. Serrano, M.C. Gutiérrez, M.L. Ferrer, F. del Monte, Deep-eutectic solvents playing multiple
479 roles in the synthesis of polymers and related materials, *Chem. Soc. Rev.*, 41 (2012)
480 4996-5014.<https://doi.org/10.1039/C2CS15353J>.

481

482 [24] M. Francisco, A. van den Bruinhorst, M.C. Kroon, Low - transition - temperature mixtures (LTTMs): A new
483 generation of designer solvents, *Angew. Chem. Int. Ed.*, 52 (2013) 3074-3085.<https://doi.org/10.1002/anie.201207548>.

484

485 [25] D. Yang, M. Hou, H. Ning, J. Zhang, J. Ma, G. Yang, B. Han, Efficient SO₂ absorption by renewable choline
486 chloride-glycerol deep eutectic solvents, *Green Chem.*, 15 (2013) 2261-2265.<https://doi.org/10.1039/C3GC40815A>.

487

488 [26] D. Yu, T. Mu, Strategy To Form Eutectic Molecular Liquids Based on Noncovalent Interactions, *J. Phys. Chem.*
489 *B* 123 (2019) 4958-4966. <https://doi.org/10.1021/acs.jpcc.9b02891>.

490

491 [27] D. Yu, H. Mou, X. Zhao, Y. Wang, T. Mu, Eutectic Molecular Liquids Based on Hydrogen Bonding and π - π
492 Interaction for Exfoliating Two-dimensional Materials and Recycling Polymers, *Chemistry – An Asian Journal*, 14
493 (2019) 3350-3356. <https://doi.org/10.1002/asia.201900990>.

494

495 [28] D. Yu, H. Mou, H. Fu, X. Lan, Y. Wang, T. Mu, "Inverted" Deep Eutectic Solvents Based on Host-Guest
496 Interactions, *Chem. Asian J.*, 14 (2019) 4183-4188. <https://doi.org/10.1002/asia.201901365>.

497

498 [29] M. Momotko, J. Łuczak, A. Przyjazny, G. Boczkaj, First deep eutectic solvent-based (DES) stationary phase
499 for gas chromatography and future perspectives for DES application in separation techniques, *J. Chromatogr. A*,
500 1635 (2021) 461701. <https://doi.org/10.1016/j.chroma.2020.461701>.

501

502 [30] A.R. Harifi-Mood, F. Mohammadpour, G. Boczkaj, Solvent dependency of carbon dioxide Henry's constant in
503 aqueous solutions of choline chloride-ethylene glycol based deep eutectic solvent, *J. Mol. Liq.*, 319 (2020)
504 114173. <http://dx.doi.org/10.1016/j.molliq.2020.114173>.

505



506 [31] P. Makoś, A. Przyjazny, G. Boczkaj, Hydrophobic deep eutectic solvents as “green” extraction media for
507 polycyclic aromatic hydrocarbons in aqueous samples, *J. Chromatogr. A*, 1570 (2018)
508 28-37. <https://doi.org/10.1016/j.chroma.2018.07.070>.

509

510 [32] N. Faraz, H.U. Haq, M.B. Arain, R. Castro-Muñoz, G. Boczkaj, A. Khan, Deep eutectic solvent based method
511 for analysis of Niclosamide in pharmaceutical and wastewater samples—A green analytical chemistry approach, *J.*
512 *Mol. Liq.*, 335 (2021) 116142. <https://doi.org/10.1016/j.molliq.2021.116142>.

513

514 [33] P. Makoś, G. Boczkaj, Deep eutectic solvents based highly efficient extractive desulfurization of fuels—
515 Eco-friendly approach, *J. Mol. Liq.*, 296 (2019) 111916. <https://doi.org/10.1016/j.molliq.2019.111916>.

516

517 [34] S. Ullah, H.U. Haq, M. Salman, F. Jan, F. Safi, M.B. Arain, M.S. Khan, R. Castro-Muñoz, G.J.M. Boczkaj,
518 Ultrasound-Assisted Dispersive Liquid-Liquid Microextraction Using Deep Eutectic Solvents (DESs) for Neutral
519 Red Dye Spectrophotometric Determination, *Molecules*, 27 (2022) 6112. <https://doi.org/10.3390/molecules27186112>.

520

521 [35] F. Elahi, M.B. Arain, W. Ali Khan, H. Ul Haq, A. Khan, F. Jan, R. Castro-Muñoz, G. Boczkaj,
522 Ultrasound-assisted deep eutectic solvent-based liquid–liquid microextraction for simultaneous determination of
523 Ni (II) and Zn (II) in food samples, *Food Chem.*, 393 (2022) 133384. <https://doi.org/10.1016/j.foodchem.2022.133384>.

524



525 [36] H.U. Haq, M. Balal, R. Castro-Muñoz, Z. Hussain, F. Safi, S. Ullah, G. Boczkaj, Deep eutectic solvents based
526 assay for extraction and determination of zinc in fish and eel samples using FAAS, *J. Mol. Liq.*, 333 (2021)
527 115930.<https://doi.org/10.1016/j.molliq.2021.115930>.

528

529 [37] M. Atilhan, S. Aparicio, s, , Deep eutectic solvents on the surface of face centered cubic metals, *J. Phys. Chem.*
530 *C.*, 120 (2016) 10400-10409.<https://doi.org/10.1021/acs.jpcc.6b01826>.

531

532 [38] D. González - Martínez, V. Gotor, V. Gotor - Fernández, Application of deep eutectic solvents in
533 promiscuous lipase - catalysed aldol reactions, *Eur.J.Org.Chem.*, 2016 (2016)
534 1513-1519.<https://doi.org/10.1002/ejoc.201501553>.

535

536 [39] D. Lindberg, M. de la Fuente Revenga, M. Widersten, Deep eutectic solvents (DESs) are viable cosolvents for
537 enzyme-catalyzed epoxide hydrolysis, *J. Biotechnol.*, 147 (2010) 169-171.<https://doi.org/10.1016/j.jbiotec.2010.04.011>.

538

539 [40] A. Wang, X. Zheng, Z. Zhao, C. Li, X. Zheng, Deep eutectic solvents to organic synthesis, *Prog. Chem.*, 26
540 (2014) 784.<https://doi.org/10.7536/PC131124>.

541

542 [41] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte, Natural deep eutectic solvents–solvents
543 for the 21st century, *ACS Sustain. Chem. Eng.*, 2 (2014) 1063-1071.<https://doi.org/10.1021/sc500096j>.

544



545 [42] X. Li, K.H. Row, Development of deep eutectic solvents applied in extraction and separation, *J. Sep. Sci.*, 39
546 (2016) 3505-3520. <https://doi.org/10.1002/jssc.201600633>.

547
548 [43] M. Faggian, S. Sut, B. Perissutti, V. Baldan, I. Grabnar, S. Dall'Acqua, Natural deep eutectic solvents (NADES)
549 as a tool for bioavailability improvement: pharmacokinetics of rutin dissolved in proline/glycine after oral
550 administration in rats: possible application in nutraceuticals, *Molecules*, 21 (2016)
551 1531. <https://doi.org/10.3390/molecules21111531>.

552
553 [44] M.C. Serrano, M.C. Gutiérrez, R. Jiménez, M.L. Ferrer, F. del Monte, Synthesis of novel lidocaine-releasing
554 poly (diol-co-citrate) elastomers by using deep eutectic solvents, *ChemComm.*, 48 (2012)
555 579-581. <https://doi.org/10.1039/C1CC15284J>.

556
557 [45] H.G. Morrison, C.C. Sun, S. Neervannan, Characterization of thermal behavior of deep eutectic solvents and
558 their potential as drug solubilization vehicles, *Int. J. Pharm.*, 378 (2009)
559 136-139. <https://doi.org/10.1016/j.ijpharm.2009.05.039>.

560
561 [46] S. Lawes, S. Hainsworth, P. Blake, K. Ryder, A. Abbott, Lubrication of steel/steel contacts by choline chloride
562 ionic liquids, *Tribol. Lett.*, 37 (2010) 103-110. <https://doi.org/10.1007/s11249-009-9495-6>.

563



564 [47] N. Guajardo, C.R. Müller, R. Schrebler, C. Carlesi, P. Dominguez de Maria, Deep eutectic solvents for
565 organocatalysis, biotransformations, and multistep organocatalyst/enzyme combinations, *ChemCatChem*, 8 (2016)
566 1020-1027. <https://doi.org/10.1002/cctc.201501133>.

567

568 [48] A. Abo-Hamad, M. Hayyan, M.A. AlSaadi, M.A. Hashim, Potential applications of deep eutectic solvents in
569 nanotechnology, *Chem. Eng. J.*, 273 (2015) 551-567. <https://doi.org/10.1016/j.cej.2015.03.091>.

570

571 [49] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Natural deep eutectic solvents as new
572 potential media for green technology, *Anal. Chim. Acta*, 766 (2013) 61-68. <https://doi.org/10.1016/j.aca.2012.12.019>.

573

574 [50] A. Worth, A. Bassan, E. Fabjan, A. Gallegos Saliner, T. Netzeva, G. Patlewicz, M. Pavan, I. Tsakovska, The
575 Use of Computational Methods in the Grouping and Assessment of Chemicals-Preliminary Investigations, in: J
576 Office for Official Publications of the European Communities, Luxembourg, 2007.

577 [51] M. Jablonsky, A. Skulcova, A. Haz, J. Sima, V. Majová, Long-term isothermal stability of deep eutectic
578 solvents, *BioResources*, 13 (2018) 7545-7559. <http://dx.doi.org/10.15376/biores.13.4.7545-7559>.

579

580 [52] H. El Shayeb, F. El Wahab, S.Z. El Abedin, Effect of some phenols on corrosion of Al, Cu, and Al-Cu alloys in
581 NaOH solutions, *Br. Corros. J.*, 34 (1999) 145-150. <https://doi.org/10.1179/000705999101500798>.

582

583 [53] H. Ren, S. Lian, X. Wang, Y. Zhang, E. Duan, Exploiting the hydrophilic role of natural deep eutectic solvents
584 for greening CO₂ capture, *J. Clean. Prod.*, 193 (2018) 802-810. <https://doi.org/10.1016/j.jclepro.2018.05.051>.

585

586 [54] J. Wang, H. Cheng, Z. Song, L. Chen, L. Deng, Z. Qi, Carbon dioxide solubility in phosphonium-based deep
587 eutectic solvents: an experimental and molecular dynamics study, *Ind. Eng. Chem. Res.* , 58 (2019)
588 17514-17523.<https://doi.org/10.1021/acs.iecr.9b03740>.

589

590 [55] H. Wibowo, L. Zhong, Q. Huan, Q. Hu, D.A. Rahim, M. Yan, Experimental study on the effect of water
591 addition to ChCl-MEA DES towards its performance in CO₂ removal from syngas, *Biomass Convers. Biorefin.*, 12
592 (2022) 61-71.<https://doi.org/10.1007/s13399-021-01673-w>.

593

594 [56] S.K. Shukla, J.-P. Mikkola, Intermolecular interactions upon carbon dioxide capture in deep-eutectic solvents,
595 *Phys. Chem. Chem. Phys.*, 20 (2018) 24591-24601.<https://doi.org/10.1039/C8CP03724H>.

596 [57] X. Liu, B. Gao, Y. Jiang, N. Ai, D. Deng, Solubilities and thermodynamic properties of carbon dioxide in
597 guaiacol-based deep eutectic solvents, *J. Chem. Eng. Data.*, 62(2017) 1448-1455.<https://doi.org/10.1021/acs.jced.6b01013>.

598 [58] *Phenol: Health Hazard Information.*, (online).US Environmental Protection Agency, April
599 1992,<https://www.epa.gov/sites/default/files/2016-09/documents/phenol.pdf>; (27 June 2022).

600 [59] *Diethylene glycol: Toxicological Evaluation.*, (online).Scientific Committee on Consumer Products SCCP, 24 June
601 2008,https://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_139.pdf; (27 June 2022).

602 [60] Mono ethanolamine: Hazard Summary. , (online).New Jersey department of health and senior services, June
603 1996,<https://www.nj.gov/health/eoh/rtkweb/documents/fs/0835.pdf>; (27 June 2022).

604 [61] Ethylenediamine: Hazard Summary., (online).New Jersey department of health and senior services, March
605 1995,<https://www.nj.gov/health/eoh/rtkweb/documents/fs/0875.pdf>; (27 June 2022).

- 606 [62] Guaiacol 99+%, 23 July 1998,<https://fscimage.fishersci.com/msds/06742.htm> (30 July 2022).
- 607 [63] N. De Arespacochaga, C. Valderrama, C. Mesa, L. Bouchy, J. Cortina, Biogas deep clean-up based on
608 adsorption technologies for Solid Oxide Fuel Cell applications, *Chem. Eng. J.*, 255 (2014)
609 593-603.<https://doi.org/10.1016/j.cej.2014.06.072>.
- 610 [64] B. Hernández, M. Martín, Optimal composition of the biogas for dry reforming in the production of methanol,
611 *Ind. Eng. Chem. Res.*, 55 (2016) 6677-6685.<https://doi.org/10.1021/acs.iecr.6b01044>.
- 612 [65] J. Zhou, X. Cao, X.-y. Yong, S.-y. Wang, X. Liu, Y.-l. Chen, T. Zheng, P.-k. Ouyang, Effects of various factors
613 on biogas purification and nano-CaCO₃ synthesis in a membrane reactor, *Ind. Eng. Chem. Res.*, 53 (2014)
614 1702-1706.<https://doi.org/10.1021/ie4034939>.
- 615
- 616 [66] V. Vrbová, K. Ciahotný, Upgrading biogas to biomethane using membrane separation, *Energ. Fuels*, 31 (2017)
617 9393-9401.<https://doi.org/10.1021/acs.energyfuels.7b00120>.
- 618
- 619 [67] O.W. Awe, Y. Zhao, A. Nzihou, D.P. Minh, N. Lyczko, A review of biogas utilisation, purification and
620 upgrading technologies, *Waste Biomass Valori.*, 8 (2017) 267-283.<https://doi.org/10.1007/s12649-016-9826-4>.
- 621
- 622 [68] F.M. Baena-Moreno, M. Rodríguez-Galán, F. Vega, L.F. Vilches, B. Navarrete, Recent advances in biogas
623 purifying technologies, *Int. J. Green Energy*, 16 (2019) 401-412.<https://doi.org/10.1080/15435075.2019.1572610>.
- 624



- 625 [69] C. Ma, C. Liu, X. Lu, X. Ji, Techno-economic analysis and performance comparison of aqueous deep eutectic
626 solvent and other physical absorbents for biogas upgrading, *Appl. Energy*, 225 (2018)
627 437-447, <https://doi.org/10.1016/j.apenergy.2018.04.112>.
- 628
- 629 [70] Y. Xie, J. Björkmalm, C. Ma, K. Willquist, J. Yngvesson, O. Wallberg, X. Ji, Techno-economic evaluation of
630 biogas upgrading using ionic liquids in comparison with industrially used technology in Scandinavian anaerobic
631 digestion plants, *Appl. Energy*, 227 (2018) 742-750, <https://doi.org/10.1016/j.apenergy.2017.07.067>.
- 632
- 633 [71] E. Słupek, P. Makoś, J. Gębicki, A. Rogala, Purification of model biogas from toluene using deep eutectic
634 solvents, in, E3S Web Conf. International Conference on Advances in Energy Systems and Environmental
635 Engineering (ASEE19), 2019, pp. 00078.
- 636 [72] E. Słupek, P. Makoś, J. Gębicki, Theoretical and economic evaluation of low-cost deep eutectic solvents for
637 effective biogas upgrading to bio-methane, *Energies*, 13 (2020) 3379, <https://doi.org/10.3390/en13133379>.
- 638
- 639 [73] Butyric acid: Health Hazard Information., (online).New Jersey department of Health, August
640 1998, <https://www.nj.gov/health/eoh/rtkweb/documents/fs/0300.pdf>; (27 June 2022).
- 641 [74] Ethylene glycol: Signs/symptoms., (online).Center for diseases control and protection, October 20,
642 2021, https://www.cdc.gov/niosh/ershdb/emergencyresponsecard_29750031.html#:~:text=Ethylene%20glycol%20h
643 [as%20a%20sweet,ingesting%20enough%20can%20cause%20death.](https://www.cdc.gov/niosh/ershdb/emergencyresponsecard_29750031.html#:~:text=Ethylene%20glycol%20has%20a%20sweet,ingesting%20enough%20can%20cause%20death;); (27 June 2022).
- 644 [75] Methacrylic Acid: Hazard Summary., (online).New Jersey department of health and senior services,
645 September 1996, <https://nj.gov/health/eoh/rtkweb/documents/fs/1277.pdf>; (28 June 2022).

646 [76] G.P. Towler, Gas Purification, 5th edition, Arthur Kohl, Richard Nielsen. Gulf Publishing Company (1997),
647 1369 pp, £157.00, ISBN: 0 88415 220 0, in, 1998.

648 [77] Q. Luo, Q. Wang, X. Sun, H. Wu, J. Hao, L. Wei, S. Zhai, Z. Xiao, Q. An, Dual-active-sites deep eutectic
649 solvents based on imidazole and resorcinol for efficient capture of NH₃, *Chem. Eng. J.*, 416 (2021)
650 129114.<https://doi.org/10.1016/j.cej.2021.129114>.

651
652 [78] M. Gao, Y. Hou, Q. Zhang, Y. Sun, S. Ren, W. Wu, Absorption of SO₂ in simulated flue gas by functional
653 deep eutectic solvents based on imidazole and H₂O with high mass capacities, *Energ. Fuels*, 34 (2020)
654 4754-4760.<https://doi.org/10.1021/acs.energyfuels.0c00057>.

655
656 [79] I. Wazeer, M.K. Hadj-Kali, I.M. Al-Nashef, Utilization of deep eutectic solvents to reduce the release of
657 hazardous gases to the atmosphere: A critical review, *Molecules*, 26 (2020)
658 75.<https://doi.org/10.3390/molecules26010075>.

659
660 [80] V. Danielik, J. Jurišová, P. Fellner, R. Štefancová, M. Kučera, Absorption of ammonia in the melt of
661 ammonium nitrate, *Chem. Pap.*, 72 (2018) 3119-3128.<http://dx.doi.org/10.1007/s11696-018-0541-4>.

662
663 [81] M. Higa, E.Y. Yamamoto, J.C.D. de Oliveira, W.A.S. Conceição, Evaluation of the integration of an
664 ammonia-water power cycle in an absorption refrigeration system of an industrial plant, *Energy Convers. Manag.*,
665 178 (2018) 265-276.<https://doi.org/10.1016/j.enconman.2018.10.041>.

666



667 [82] R. Sander, Compilation of Henry's law constants (version 4.0) for water as solvent, *Atmos. Chem. Phys.*, 15
668 (2015) 4399-4981, <https://doi.org/10.5194/acp-15-4399-2015>.

669

670 [83] V. Kaplan, E. Wachtel, I. Lubomirsky, Carbonate melt regeneration for efficient capture of SO₂ from coal
671 combustion, *RSC Adv.*, 3 (2013) 15842-15849, <https://doi.org/10.1039/C3RA42654H>.

672

673 [84] K. Zhang, S. Ren, Y. Hou, W. Wu, Efficient absorption of SO₂ with low-partial pressures by environmentally
674 benign functional deep eutectic solvents, *J. Hazard. Mater.*, 324 (2017)
675 457-463, <https://doi.org/10.1016/j.jhazmat.2016.11.012>.

676

677 [85] W.-J. Jiang, F.-Y. Zhong, L.-S. Zhou, H.-L. Peng, J.-P. Fan, K. Huang, Chemical dual-site capture of NH₃ by
678 unprecedentedly low-viscosity deep eutectic solvents, *ChemComm.*, 56(2020)
679 2399-2402, <https://doi.org/10.1039/C9CC09043F>.

680

681 [86] Resorcinol: Health Hazard Information., (online).New Jersey department of Health, June
682 2001, <https://www.nj.gov/health/eoh/rtkweb/documents/fs/1634.pdf>; (28 June 2022).

683 [87] Glycerol: Hazards Identification., (online).Environmental Health & Safety USA, 15 February
684 2008, <https://www.uvm.edu/~vgn/outreach/documents/GLYCEROL.pdf>; (12 September 2022).

685 [88] H.M. Lyuhong Zhang, Xiaowei Tantai, Na Yang Study on the absorption of nitric oxide by benzoic
686 acid-based deep eutectic solvents, *Chin. J. Chem. Eng.*, 71 (2020)
687 3644-3651, <https://doi.org/10.11949/0438-1157.20200116>.

688

689 [89] Benzoic acid: Health Hazard Information. , (online).New Jersey department of Health, October
690 2000,<https://www.nj.gov/health/eoh/rtkweb/documents/fs/0209.pdf>; (28 June 2022).

691 [90] S. Sun, Y. Niu, Q. Xu, Z. Sun, X. Wei, Efficient SO₂ absorptions by four kinds of deep eutectic solvents based
692 on choline chloride, *Ind. Eng. Chem. Res.*, 54 (2015) 8019-8024.<https://doi.org/10.1021/acs.iecr.5b01789>.

693

694 [91] Malonic Acid: Hazards Identification., (online).Flinn Scientific, 21 March
695 2014,https://www.flinnsci.com/sds_486-malonic-acid/sds_486/; (28 June 2022).

696 [92] U.-U.T. Vö, M.P. Morris, Nonvolatile, semivolatile, or volatile: Redefining volatile for volatile organic
697 compounds, *J. Air Waste Manag. Assoc.*, 64 (2014) 661-669.<https://doi.org/10.1080/10962247.2013.873746>.

698

699 [93] P. Makoś-Chelstowska, VOCs absorption from gas streams using deep eutectic solvents – A review, *J. Hazard.*
700 *Mater.*, 448 (2023) 130957.<https://doi.org/10.1016/j.jhazmat.2023.130957>.

701

702 [94] n-Hexane: Workplace exposure limits, (online).New Jersey department of Health, April
703 2004,<https://nj.gov/health/eoh/rtkweb/documents/fs/1340.pdf>; (21 Feb 2023).

704 [95] Benzene: Workplace exposure limits, (online).New Jersey department of Health, October
705 2008,<https://nj.gov/health/eoh/rtkweb/documents/fs/0197.pdf>; (21 Feb 2023).

706 [96] Toulene: Workplace exposure limits, (online).New Jersey department of Health, November
707 2007,<https://nj.gov/health/eoh/rtkweb/documents/fs/1866.pdf>; (21 Feb 2023).



708 [97] Xylenes: Work place exposure limits, (online).New Jersey department of Health, October
709 2014,<https://nj.gov/health/eoh/rtkweb/documents/fs/2014.pdf>; (21 Feb 2023).

710 [98] G. Boczkaj, P. Makoś, A. Przyjazny, Application of dynamic headspace and gas chromatography coupled to
711 mass spectrometry (DHS-GC-MS) for the determination of oxygenated volatile organic compounds in refinery
712 effluents, *Anal. Methods*, 8 (2016) 3570-3577.<https://doi.org/10.1039/C5AY03043A>.

713

714 [99] G. Boczkaj, A. Przyjazny, M. Kamiński, Characteristics of volatile organic compounds emission profiles from
715 hot road bitumens, *Chemosphere*, 107 (2014) 23-30.<https://doi.org/10.1016/j.chemosphere.2014.02.070>.

716

717 [100] M. Gagol, G. Boczkaj, J. Haponiuk, K. Formela, Investigation of volatile low molecular weight compounds
718 formed during continuous reclaiming of ground tire rubber, *Polym. Degrad. Stab.*, 119 (2015)
719 113-120.<https://doi.org/10.1016/j.polymdegradstab.2015.05.007>.

720

721 [101] P. Makoś, A. Przyjazny, G. Boczkaj, Methods of assaying volatile oxygenated organic compounds in effluent
722 samples by gas chromatography—A review, *J. Chromatogr. A*, 1592 (2019)
723 143-160.<https://doi.org/10.1016/j.chroma.2019.01.045>.

724

725 [102] S. Beil, M. Markiewicz, C.S. Pereira, P. Stepnowski, J. Thöming, S. Stolte, Toward the proactive design of
726 sustainable chemicals: Ionic liquids as a prime example, *Chem. Rev.*, 121 (2021)
727 13132-13173.<https://doi.org/10.1021/acs.chemrev.0c01265>.

728

729 [103] M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the Nature of Eutectic and Deep Eutectic Mixtures,
730 *J. Solut. Chem.*, 48 (2019) 962-982. <https://doi.org/10.1007/s10953-018-0793-1>.

731
732 [104] T. Lemaoui, N.E.H. Hammoudi, I.M. Alnashef, M. Balsamo, A. Erto, B. Ernst, Y. Benguerba, Quantitative
733 structure properties relationship for deep eutectic solvents using $S\sigma$ -profile as molecular descriptors, *J. Mol. Liq.*,
734 309 (2020) 113165. <https://doi.org/10.1016/j.molliq.2020.113165>.

735
736 [105] T. Lemaoui, A.S. Darwish, A. Attoui, F.A. Hatab, N.E.H. Hammoudi, Y. Benguerba, L.F. Vega, I.M. Alnashef,
737 Predicting the density and viscosity of hydrophobic eutectic solvents: Towards the development of sustainable
738 solvents, *Green Chem.*, 22 (2020) 8511-8530. <https://doi.10.1039/D0GC03077E>.

739
740 [106] T. Lemaoui, A.S. Darwish, N.E.H. Hammoudi, F. Abu Hatab, A. Attoui, I.M. Alnashef, Y. Benguerba,
741 Prediction of Electrical Conductivity of Deep Eutectic Solvents Using COSMO-RS Sigma Profiles as Molecular
742 Descriptors: A Quantitative Structure–Property Relationship Study, *Ind. Eng. Chem. Res.*, 59 (2020)
743 13343-13354. [10.1021/acs.iecr.0c02542](https://doi.org/10.1021/acs.iecr.0c02542).

744
745 [107] H. Ghaedi, M. Ayoub, S. Sufian, B. Lal, Y. Uemura, Thermal stability and FT-IR analysis of
746 Phosphonium-based deep eutectic solvents with different hydrogen bond donors, *J. Mol. Liq.*, 242 (2017)
747 395-403. <https://doi.org/10.1016/j.molliq.2017.07.016>.

748



749 [108] S.L. Perkins, P. Painter, C.M. Colina, Molecular Dynamic Simulations and Vibrational Analysis of an Ionic
750 Liquid Analogue, *J. Phys. Chem. B*, 117 (2013) 10250-10260.10.1021/jp404619x.

751

752 [109] S.L. Perkins, P. Painter, C.M. Colina, Experimental and Computational Studies of Choline Chloride-Based
753 Deep Eutectic Solvents, *J. Chem. Eng. Data*, 59 (2014) 3652-3662.10.1021/je500520h.

754

755 [110] R. Ghobadi, A. Divsalar, Enzymatic behavior of bovine liver catalase in aqueous medium of sugar based
756 deep eutectic solvents, *J. Mol. Liq.*, 310 (2020) 113207.<https://doi.org/10.1016/j.molliq.2020.113207>.

757

758 [111] V. Gotor-Fernández, C.E. Paul, Deep eutectic solvents for redox biocatalysis, *J. Biotechnol.*, 293 (2019)
759 24-35.<https://doi.org/10.1016/j.jbiotec.2018.12.018>.

760

761 [112] Z.-L. Huang, B.-P. Wu, Q. Wen, T.-X. Yang, Z. Yang, Deep eutectic solvents can be viable enzyme activators
762 and stabilizers, *J. Chem. Technol. Biotechnol.*, 89 (2014) 1975-1981.<https://doi.org/10.1002/jctb.4285>.

763

764 [113] Y.P. Mbous, M. Hayyan, A. Hayyan, W.F. Wong, M.A. Hashim, C.Y. Looi, Applications of deep eutectic
765 solvents in biotechnology and bioengineering—Promises and challenges, *Biotechnol. Adv.*, 35 (2017)
766 105-134.<https://doi.org/10.1016/j.biotechadv.2016.11.006>.

767



768 [114] A. Hayyan, F.S. Mjalli, I.M. AlNashef, T. Al-Wahaibi, Y.M. Al-Wahaibi, M.A. Hashim, Fruit sugar-based
769 deep eutectic solvents and their physical properties, *Thermochim. Acta*, 541 (2012)
770 70-75. <https://doi.org/10.1016/j.tca.2012.04.030>.

771
772 [115] J. Kim, Y. Shi, C.J. Kwon, Y. Gao, S. Mitragotri, A Deep Eutectic Solvent-Based Approach to Intravenous
773 Formulation, *Adv. Healthc. Mater.*, 10 (2021) 2100585. <https://doi.org/10.1002/adhm.202100585>.

774
775 [116] N.R. Mustafa, V.S. Spelbos, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Solubility and Stability of Some
776 Pharmaceuticals in Natural Deep Eutectic Solvents-Based Formulations, *Molecules*, 26 (2021)
777 2645. <https://doi.org/10.3390/molecules26092645>.

778
779 [117] K. Mamtani, K. Shahbaz, M.M. Farid, Deep eutectic solvents – Versatile chemicals in biodiesel production,
780 *Fuel*, 295 (2021) 120604. <https://doi.org/10.1016/j.fuel.2021.120604>.

781
782 [118] S. Anđelović, M. Božinović, Ž. Čurić, A. Šalić, A. Jurinjak Tušek, K.Z. Kučan, M. Rogošić, M. Radović, M.
783 Cvjetko Bubalo, B. Zelić, Deep Eutectic Solvents for Biodiesel Purification in a Microextractor: Solvent Preparation,
784 Selection and Process Optimization, *Bioengineering* 9(2022) 665. <https://doi.org/10.3390/bioengineering9110665>.

785

786