

Deep Eutectic Solvents and Their Uses for Air Purification

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ABSTRACT

Chemical compounds released into the air by the activities of industrial plants and emitted from many other sources, including in households (paints, waxes, cosmetics, disinfectants, plastic (PVC) flooring), may affect the environment and human health. Thus, air purification is an important issue in the context of caring for the condition of the environment. Deep eutectic solvents (DESs) as liquids with environmentally friendly properties (non-volatile, biodegradable, non-toxic, cheap, easy to prepare) are a promising solution to this problem. This paper reviews the advances made in the application of DESs as sorbents for the purification of atmospheric and indoor air. The potential of DESs and their subclasses (including SUPRAMolecular Deep Eutectic Solvents, SUPRADESs) applications in air purification processes were also summarized. The authors believe that this review can be useful for future readers as a starting point for research in the field of DESs and their application in air purification.

Keywords: volatile organic compounds, VOCs, air purification, deep eutectic solvents, sorbents.

INTRODUCTION

Civilization leads to many environmental changes. An increasing number of production plants, animal husbandry, gas stations, consumerism, the popularity of plastic products (often disposable), and numerous other factors contribute to the deterioration of the environment - including air quality. The presence of harmful gases, compounds with an irritating odor and toxic vapors in the atmospheric and indoor air is a very troublesome. The exposure to harmful gases may cause discomfort or deterioration of health (burns, skin irritation, irritation of the throat mucosa, irritation of the lungs); exposure to very high concentrations of toxic gases may even cause permanent lung damage or death (Adavan Kiliyankil et al., 2021). The World Health Organization (WHO) reports that 4.2 million people die each year from air pollution (Masic et al., 2018). Moreover, 99%

of the world's population breathes air in excess of the limits set by the WHO guidelines (Air Pollution, 2022). The pollution in the air affects the degradation of the ozone layer and is harmful to flora and fauna. The people living close to emission sources are exposed to the compounds emitted daily. It is predicted that by 2100 the world's population will be 80% urbanized (in Europe, the degree of urbanization will be as high as 90%) (Bank et al., 2019). Due to the expected significant increase in exposure, air purification is an important issue, because it determines the comfort of human life and their safety.

Odor and harmful compounds in the air are mainly derivatives of ammonia, nitrogen oxides, aliphatic and aromatic hydrocarbons, hydrogen sulfide, sulfur dioxide, thiols (aliphatic and aromatic mercaptanamines) and carbon dioxide (CO₂) (Adavan Kiliyankil et al., 2021). Odors are a numerous group of compounds characterized

by a strong irritating, unpleasant odor; however, their unpleasant smell is not their main problem – they rank second among the seven major environmental threats (Y. Liu et al., 2020).

The proposed solutions to the problem of air pollution with harmful chemical compounds have recently been based mainly on the use of sorbents such as activated carbon (Ahammad S. Z.; Gomes J.; Sreekrishnan, 2008; Aygün et al., 2003; Gratuito et al., 2008; Heidarinejad et al., 2020), silica gel (Banerjee et al., 2001; Oszust et al., 2012; Zallama et al., 2018) or zeolites (Król 2020; Moutsatsou et al., 2006). These sorbents, despite their wide application, have certain disadvantages. For activated carbon (obtained by the physical activation method), there is a relatively low adsorption capacity, in addition, the material activation process is very long and requires a large amount of energy during production (Yahya et al., 2015). The activated carbon obtained in the process of chemical activation is a sorbent with a small pore size and a large specific surface area, but a significant disadvantage of this adsorbent is the use of environmentally harmful chemicals during its production (such as phosphoric acid or (in order to obtain a material with a larger specific surface area) zinc chloride) (Heidarinejad et al., 2020). Silica gel, likewise, requires the use of chemicals in the synthesis process. For natural zeolites, a significant disadvantage is the need for activation and packaging of raw material. Therefore, the preparation of the sorbent can be very expensive. Synthesis of synthetic zeolites (which are more homogeneous than natural zeolites and enable the adjustment of physicochemical properties to a specific application) requires the use of chemicals, i.e. organic bases and/or alkali hydroxides (Petrov et al., 2012).

The 12 Green Chemistry principles introduced by Anastas and Warner in 1998 (Warner et al., 1998) and the principles of Green Analytical Chemistry (Tobiszewski et al., 2010) increased the interest of the scientific community in looking for green alternatives to the previously known solutions of analytical and industrial processes. Advances in greening processes have increased the pace of research on ionic liquids (ILs) (García et al., 2015; Holbrey et al., 1999; Jenkins 2011; Lei et al., 2017; Swatloski et al., 2002). The toxic nature of many components used in the synthesis of ILs was demonstrated in later years (Pretti et al., 2006; Zhao et al., 2007) and their detrimental effect on living organisms (Bubalo et al., 2017)

has made their use questionable. Apart from their advantages, conventional sorbents and ILs have significant disadvantages, so it is important to consider and investigate green and more effective alternatives. One of the most popular green alternatives was described in 2003 (Abbott et al., 2003). Deep Eutectic Solvents (DESs) are currently one of the most promising solutions to improve many processes (both on the analytical and process scale).

DEEP EUTECTIC SOLVENTS (DESs)

DESs are amazing liquids created through the interaction between two components (most often solid at room temperature) based mainly on the formation of hydrogen bonds. One component is a hydrogen bond donor (HBD) and the other acts as an acceptor (Hydrogen Bond Acceptor, HBA) (Janicka et al., 2021). The ability to create hydrogen bonds by individual compounds is closely related to their structure (the presence of functional groups capable of donor-acceptor interactions). The formation of bonds between the DES components leads to a significant decrease in the melting point of the mixture. An important and often overlooked issue is that not all solvents generated as a result of HBD-HBA interactions show a significant drop in melting point compared to pure ingredients used for their synthesis, i.e. those that do not deviate significantly from ideal predictions should be referred to as eutectic solvents (ES) (Andruch et al., 2022).

DESs described by Abbott et al. were obtained by combining choline chloride with urea and choline chloride with carboxylic acids (Abbott et al., 2003). Most of the DESs known so far are also synthesized with the use of environmentally friendly, non-toxic, non-volatile, non-flammable and cheap substances, and the synthesis process is very simple and inexpensive; the most common synthesis takes place while mixing the ingredients with heating.

DESs are of high interest and are applied in many research areas as well as industrial processes (Fig. 1). As green alternatives to the commercially used toxic solvents, DESs have been successfully employed in many processes e.g. as absorbents for effective removal of the main impurities from biogas streams (Słupek et al., 2020), in extractive detoxification of feedstocks for the production of biofuels (Makoś et al., 2020a), in

analytical chemistry as effective and selective extractants (Abouheif et al., 2022; Baute-Pérez et al., 2022; Kalyniukova et al., 2021; Nia et al., 2021; Pan et al., 2021), in delignification process (Jablonsky et al., 2018), in chemical synthesis for the alkylation/arylation of ketones (Vidal et al., 2014) and in many other processes (Figure 1) (Kalyniukova et al., 2021; Percevault et al., 2021; Płotka-Wasyłka et al., 2017; Smith et al., 2014; Tang et al., 2015; Zhang et al., 2012).

There are several subgroups of DES including the following: i) Natural Deep Eutectic Solvents (NADES) which is synthesized from ingredients of natural origin (such as sugars, sugar alcohols, organic acids and amino acids) (Dai et al., 2013; Faggian et al., 2016; Paiva et al., 2014) - NADESs are highly biodegradable and non-toxic; ii) Hydrophobic Deep Eutectic Solvents (HDESs) (Makoś et al., 2020b) which show hydrophobic properties; iii) Natural Hydrophobic Deep Eutectic Solvents (NAHDESs), in addition to their hydrophobic properties, have, as has previously been mentioned in the context of NADESs, a natural composition (Baute-Pérez,

et al., 2022); iv) Therapeutic Deep Eutectic Solvents (THEDESs) – which have bioactive properties; v) Amino Acid-Based Natural Deep Eutectic Solvents – DESs based on amino acids; vi) Supramolecular Deep Eutectic Solvents (SUPRADESs) (Janicka et al., 2022), which are based on cyclodextrins. The latter, SUPRADESs, are distinguished by unique properties that should be emphasized. Due to cyclodextrins as a key ingredient, SUPRADESs have the unusual ability to bind numerous compounds through DESs-specific interactions (hydrogen bonding) and through host-guest interactions typical of cyclodextrins (Figure 2).

The unique properties of DES make them very popular, especially in the context of greening industrial and analytical processes. They are undoubtedly one of the most important discoveries in the field of Green Chemistry. Due to the green nature and the ability to interact with numerous substances, DESs are an interesting novelty, which may turn out to be more cost-effective compared to the sorbents used so far.

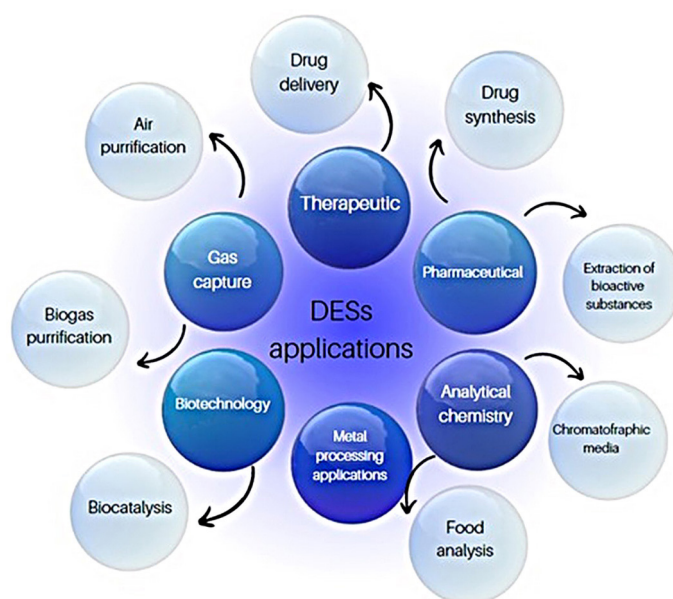


Figure 1. Applications of deep eutectic solvents

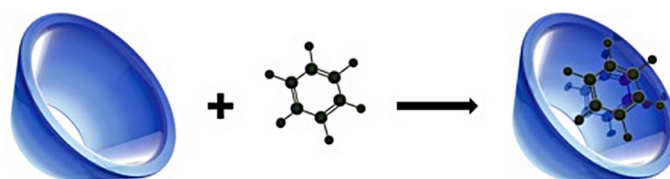


Figure 2. Inclusion complex formation

Deep eutectic solvents as a sorbents for air purification

Removing odors and toxic compounds from the air is a very important task due to their negative impact on the quality of life and health of humans and animals. However, the effective, economic, selective and permanent elimination of undesirable compounds from the air is a major challenge. Numerous technologies have been developed to air purification, but these techniques are often limited by the production of harmful by-products and the use of toxic solvents (Krishnan et al., 2020). The use of sorbents which are cheap, biodegradable, easy to prepare, non-toxic and stable at elevated temperature, and the production of which does not generate waste, is a solution that meets the assumptions of Green Chemistry. Deep Eutectic Solvents are a promising alternative with high potential for green process applications. Numerous tests of DESs capacity and the confirmed ability to regenerate are the basis for the ecologically beneficial transformation of many technological processes. Due to the galloping climatic changes, the use of an ecological medium to absorb harmful gases from the air, is a promising breakthrough. The available literature on the use of DESs as absorbents is extensive.

Absorptive binding of harmful gases by deep eutectic solvents

NH_3 absorption

Ternary DESs with the ethanolamine hydrochloride composition: resorcinol: glycerol (EACl: Res: Gly; molar ratio 1: 4: 5) was tested as ammonia absorbent (Luo et al., 2021). Luo et al. showed in their research work that EACl: Res: Gly has a high absorption capacities (up to 0.240 g/g in 293.15 K and pressure 0.10 MPa) compared to other DES and ILs described in the literature (Table 1). For similar pressure and temperature conditions, DESs show a much higher absorption capacity compared to zeolite 13X. The high efficiency of NH_3 uptake by EACl: Res: Gly (1: 4: 5) is due to the strong interactions based on the formation of hydrogen bonds between NH_3 and DESs. The described DESs also showed high thermal stability, which is an additional advantage (it enables multiple use of the solvent, positively influencing the ecological and economic aspects of the process). The use of NADES choline chloride: xylose (molar ratio 1.5: 1) at a

temperature of 343.15K and a pressure of 0.1013 MPa allowed obtaining a very high efficiency of capturing NH_3 – up to 3.884 mol/kg (Table 1). Described NADESs exhibit higher NH_3 capacities in comparison to most other sorbents reported in the literature (Li et al., 2020). The increase in absorption efficiency under elevated temperature conditions is related to a significant decrease in the viscosity of NADESs under the influence of temperature increase. The great advantage of this solvent is its extremely safe composition; both choline chloride and xylose used in the synthesis of the above-mentioned NADESs are the components that are completely safe for the environment and living organisms.

DES described by Jiang et al. composed of ethylamine hydrochloride and glycerol (molar ratio 1: 2) had extremely high absorption capacity for ammonia (Jiang et al., 2019) – the highest capacity (16.538 mol/kg) was achieved for the temperature conditions of 333.15K and the pressure of 0.2407 MPa. The absorption efficiency was mainly influenced by the NH_3 pressure value – the molar ratio of the components and the temperature did not significantly affect the efficiency of the process. DESs absorption capacity significantly exceeds the results obtained for ILs (Table 1).

SO_2 absorption

Yang et al. examined the use of NADESs composed of choline chloride (ChCl) and glycerol (molar ratios 1: 1, 1: 2, 1: 3, 1: 4) in SO_2 absorption process. The efficiency of the process was mainly influenced by the mole fraction of choline chloride in NADESs (Table 2). With an increase in the mole fraction of ChCl, a significant increase in the absorption capacity of NADESs was observed (Yang et al., 2013) (Table 2) – up to 0.678 $\frac{g_{gas}}{g_{absorbent}}$. The NADESs used in the cited work could be used at least five times in the absorption/desorption cycles. Desorption was easily achieved by reducing the partial pressure of SO_2 .

CO_2 absorption

An efficient and very ecological absorbent in the process of CO_2 absorption is NADESs with the composition of choline chloride: urea (molar ratios 1: 1.5 and 1: 2) (Table 3.). The great advantage of this solvent is its natural character, ease of preparation and high fluidity at room temperature. The available literature

Table 1. Comparison of ammonia (NH₃) absorption efficiencies for selected sorbents

Sorbent		Temp [K]	P [MPa]	NH ₃ capacity [g _{gas} /g _{sorbent}]	Ref.
Solvent	Molar ratio				
EACl: Res: Gly	1: 1: 5	313.15	0.1013	0.149	[50]
EACl: Res: Gly	1: 4: 5	313.15	0.1013	0.181	[50]
EACl: Res: Gly	1: 4: 5	293.15	0.1013	0.240	[50]
13X zeolite	-	298.15	0.1000	0.153	[51]
13X zeolite	-	298.15	0.0938	0.159	[51]
[EtOHmim][BF ₄]	-	313.15	0.1000	0.037	[52]
[Choline][NTf ₂]	-	313.15	0.1000	0.026	[52]
Sorbent		Temp [K]	P [MPa]	NH ₃ capacity [mol/kg]	Ref.
Solvent	Molar ratio				
ChCl: Xyl	1.5: 1	333.15	0.0181	1.803	[53]
ChCl: Xyl	1.5: 1	343.15	0.0140	1.745	[53]
ChCl: Xyl	1.5: 1	343.15	0.1013	3.884	[53]
EaHCl: Gly	1: 2	313.15	0.0044	0.777	[54]
EaHCl: Gly	1: 2	333.15	0.1067	9.631	[54]
EaHCl: Gly	1: 2	333.15	0.2407	16.538	[54]
EaHCl: Gly	1: 5	333.15	0.1015	9.443	[54]
[EtOHmim][NTf ₂]	-	343.15	0.1013	0.799	[55]
[Bim][NO ₃]	-	333.15	0.0180	0.897	[56]
[Mmim][NTf ₂]	-	313.15	0.0145	2.527	[56]

Note: EACl, ethanolamine; Res, resorcinol; Gly, glycerol; [EaHCl], ethylamine hydrochloride; [EtOHmim][BF₄], 1-2-(hydroxyethyl)-3-methylimidazolium tetrafluoroborate; [Choline][NTf₂], choline bis(trifluoromethylsulfonyle) imide; ChCl, cholinechloride; Xyl, xylose; EAHCl, ethylaminehydrochloride; [EtOHmim][NTf₂], 1-2-(hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyle)imide; [Bim][NO₃], 1-butylimidazolium nitrate; [Mmim][NTf₂], 1, 2-dimethylimidazolium bis(trifluoromethylsulfonyle)imide.

Table 2. Comparison of sulfur dioxide (SO₂) sorption efficiencies for selected sorbents

Sorbent		Temp [K]	P [MPa]	SO ₂ capacity [g _{gas} /g _{sorbent}]	Ref.
Solvent	Molar ratio				
ChCl: Gly	1: 1	293.15	0.0101	0.153	[57]
ChCl: Gly	1: 4	293.15	0.0101	0.046	[57]
ChCl: Gly	1: 1	293.15	0.1013	0.678	[57]
ChCl: Gly	1: 4	293.15	0.1013	0.320	[57]
Ac: AmmTh	3: 1	293.15	0.1000	1.375	[58]
Cap: Imi	1: 1	303.15	0.1000	1.660	[59]
Cap: Ac	1: 1	303.15	0.1000	0.998	[59]
ChCl: Mal	1: 1	293.15	0.1000	0.490	[60]

Note: ChCl, choline chloride; Gly, glycerol; Ac, acetamide; AmmTh, ammoniumthiocyanate; Cap, caprolactam; Imi, imidazole, Mal, malonic acid; KSCN, potassium thiocyanate.

shows that NADESs (syringol: levulinic acid in a 1: 1 molar ratio) has a high ability to absorb volatile organochlorine compounds from biogas (Makoś et al., 2020). Under optimal conditions (293.15 K, 0.010 MPa), the absorption capacity of dichloromethane, chloroform, carbon tetrachloride, 1,1,2,2-tetrachloroethane and 2,2,2-trichloroethanol was 304, 420, 360, 292

and 661 mg/g. The described NADESs can be used at least ten times in the absorption-desorption cycles. The high absorption capacity of solvent was due to hydrogen and van der Waals interactions. The simplicity of the developed process, the naturalness of the solvent used and the efficiency of the process enable it to fully meet the expectations of green processes.

Table 3. Comparison of carbon dioxide (CO₂) sorption efficiencies for selected sorbents

Sorbent		Temp [K]	P [MPa]	CO ₂ capacity [mol _{gas} /mol _{sorbent}]	Ref.
Solvent	Molar ratio				
ChCl: LacA	1: 2	75	1.927	0.0248	[62]
Sorbent		Temp [K]	P [MPa]	CO ₂ capacity [mmol _{gas} /g _{sorbent}]	Ref.
Solvent	Molar ratio				
ChCl: TeG	4: 1	293.15	0.500	0.1941	[63]
ChCl: DeG	4: 1	293.15	0.500	0.1852	[63]
ChCl: U	1: 1.5	313.15	11.840	2.7380	[64]
ChCl: U	1: 1.5	323.15	12.520	2.5696	[64]
ChCl: U	1: 1.5	333.15	12.500	2.2609	[64]
ChCl: U	1: 2	313.15	12.500	5.1646	[64]
ChCl: U	1: 2	323.15	11.100	4.2934	[64]
ChCl: U	1: 2	333.15	12.730	4.2721	[64]
ChCl: U	1:2	303.15	5.654	3.5592	[64]

Note: ChCl, choline chloride; LacA, lactic acid; TeG, triethylene glycol; DeG, diethylene glycol; U, urea.

Adsorptive binding of harmful gases by deep eutectic solvents

DESs can be used as modifiers for classic sorbents (e.g. silica gel or activated carbon). Makoš et al. impregnated silica gel with DESs (including tetrapropylammonium bromide: levulinic acid 1: 3, tetrapropylammonium bromide: lactic acid 1: 2, and choline chloride: levulinic acid 1: 2). The impregnation of the silica gel contributed to a significant increase in the efficiency of the BTEX (benzene, toluene, ethylbenzene, and p-xylene) adsorption process. For 300 mg/m³ initial concentration of BTEX in optimal conditions adsorption capacity value for pure silica gel is 43.1, while for DES-impregnated silica gel (by DES tetrapropylammonium bromide: lactic acid (1: 2)) is much higher – 254.9. Research has shown the great potential of DESs as modifiers of solid sorbents.

Potential of SUPRADESs for gas capturing by hydrogen bonding and host-guest interactions

In the context of air purification, SUPRAMOLECULAR Deep Solvents Eutectic Solvents (SUPRADESs) as a novel type of DESs should also be mentioned. SUPRADESs show a high potential for use as sorbents. The key ingredient of SUPRADESs, i.e. CDs, gives them unusual properties. CDs have a hydrophobic cavity and a hydrophilic outer surface. CDs form inclusion complexes with non-polar molecules in aqueous solutions. This property means that CDs have found numerous applications (Brewster, et al., 2007;

Buschmann, et al., 2002). The unusual structure of CDs makes them successfully used as an efficient absorbent of volatile organic compounds (VOCs) [56][57], but their high price makes it worth considering using them in the form of SUPRADESs or SUPRADESs modified sorbent. SUPRADESs as a mixture combining of CDs ability to bind multiple compounds through host-guest interactions and the DESs ability to create hydrogen bonds with many substances could be a breakthrough in air purification. Unfortunately, there is very little research into the use of SUPRADESs as sorbents for harmful gases. This research area has great potential, and we intend to investigate SUPRADESs as green sorbents in the future.

CONCLUSIONS

Deep eutectic solvents show great potential for applications. The quoted research results indicate that they allow for the design of green, cheap and often more effective processes than those known so far. The possibility of combining a wide range of ingredients, easy influence on the properties of DESs by means of temperature, the green nature of most of the ingredients used for their synthesis, the possibility of using them to modify solid sorbents and the proven effectiveness of these solvents offer great opportunities for improvement and greening of numerous processes. The use of environmentally friendly and effective sorbents for air purification is a very accurate response to the requirements of Green Chemistry.

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