**Review of green designer deep eutectic solvents (DESs) production and prospective material science applications**

Benvikram Barmana and Manoj Kumar Banjareb

MATS School of Sciences, MATS University, Pagaria Complex, Pandri, Raipur (C.G.), 492004, India

Abstract

Deep eutectic solvents (DESs) and closely related ionic liquids (ILs) have gained recognition as green and sustainable solvents because of their low cost, non-toxicity, and recyclable characteristics. With advantages including reusability, biodegradability, nontoxicity, widespread availability, low vapour pressure, low flammability, and ease of manufacturing, DESs are being lauded as potential alternatives to conventional organic solvents. These solvents are created when an organic salt, such as ammonium or phosphonium, reacts with a hydrogen-bond donor, such as an acid, an amide, or an alcohol (choline chloride and either urea or glycerol). Affordable, green, and easy-to-handle solvents are basically nonexistent right now. DESs are consequently receiving more and more interest in a number of scientific fields. The main uses of this novel family of solvents, the DESs, are covered in this review along with their synthesis.

Keywords: Deep eutectic solvents, Properties, Application, Future scope.

**1. Introduction**

Deep eutectic solvents (DESs) are a class of long-lasting, environmentally friendly, and biodegradable solvents. Ionic liquids (ILs) are a novel class of solvents that are less expensive and harmful than deep eutectic solvents (DESs) [1-2]. In order to create deep eutectic solvents (DESs), two harmless, naturally occurring, affordable, renewable, environmentally friendly, and biodegradable components must be combined [3–4]. In the beginning, researchers focused on creating ionic liquids by mixing quaternary ammonium salts (QASs) with metal salts, especially aluminium, iron, zinc, tin, and chlorides. Despite having high melting points, both salts can be properly aggregated to form a eutectic liquid phase mixture [5–6]. A large freezing point dip, typically greater than 150 0C, is a defining feature of these eutectic mixtures. The ability to chemically alter the cationic moiety with a variety of anions allows chemists to produce a wide variety of ILs with various physical properties, such as freezing point, solubility, viscosity, density, conductivity, physical phenomena, and refractivity. DESs have established a reputation as a promising solvent.

**2. Definition of DESs**

In order to create a deep eutectic solvent (DESs), two or three biodegradable and ecologically friendly components must be able to aggregate with one another through hydrogen bond interactions [7]. Deep eutectic solvents (DESs) contain nonsymmetric ions that have low lattice energy, low melting temperatures, low vapour pressure, strong electrical conductivity, good conductivity, non-volatile nature, and both good thermal stability [8].

**3. Synthesis of deep eutectic solvents**

By combining a quaternary ammonium salt with a hydrogen bond donor (HBD) or metal salts that can form a complex with the quaternary ammonium salt's halide anion, a deep eutectic solvent (DESs) is produced. Due to charge delocalization brought on by hydrogen bonding between the halide ion and therefore the hydrogen-donor moiety, the combination's freezing point is lower than the melting temperatures of the individual components [9]. The chemical that is most usually used to make deep eutectic solvents (DESs) is choline chloride (ChCl). Choline chloride (ChCl) is a quaternary ammonium salt that may be easily synthesised from fossil deposits (million metric tonnes) or recovered from biomass [10]. It is inexpensive, non-toxic, biodegradable, and ecologically benign. When ChCl aggregates with safe hydrogen bond donors like urea, renewable carboxylic acids (like oxalic acid, citric acid, succinic acid, or amino acids), or renewable polyols (like glycerol, polysaccharides), they can create a deep eutectic solvent (DES). Nuclear magnetic resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR) techniques were used to confirm the production of eutectics and hydrogen bonding in deep eutectic solvents (DESs) [11]. Fourier Transform Infrared Spectroscopy (FTIR) spectra show changes in the representative peaks and broadening of the implicated bonds, and 1H-NMR (protium nuclear magnetic resonance) spectra show changes in the resonance signal up field.



Fig: Synthesis of DESs

|  |  |
| --- | --- |
| Halide Salts | Hydrogen Bond Donors |
|  |  |
| Scheme 1: The chemical structure of Halide Salts and Hydrogen Bond Donors |

**4. Physicochemical characters of DESs**

Different quaternary ammonium salts (QASs), such as ChCl, and various hydrogen bond donors (HBD) are mixed in a specific ratio to produce deep eutectic solvents (DESs). Physicochemical characteristics of deep eutectic solvents (DESs) include conductivity, pH, viscosity, surface tension, phase behaviour, and freezing point. This section will look at the physicochemical properties of deep eutectic solvents. Sustainable technologies used in green-related material science applications should be crucial in the ensuing decades. Applications in material science, metal processing, synthetic chemistry, gas separation (CO2, SO2), tea catechin extraction, therapeutic chemistry, extraction and separation, catalyst, agroforestry, biological applications, etc., among others, play a significant part in regulating and lowering environmental pollution. Ionic liquids (ILs) may be replaced with deep eutectic solvents (DESs), which keep the majority of important characteristics like task-specific character.

**4.1. Surface tension**

Deep eutectic solvents' (DESs) surface tension is a crucial physiochemical characteristic that has applications in the fields of interface and colloid. Investigations were done into how the hydrogen-bonding donors (HBDs) and the acceptors (HBAs) affected by surface tension [12]. In addition, the surface tension of mixtures of deep eutectic solvents (DESs) and other solvents, such as water, water+ salt (such as KCl), acetone, ethanol, ethyl acetate (EtAc), isopropyl alcohol, etc. The surface tension (ST) of deep eutectic solvents (DESs) would be reduced by the inclusion of the crystal water in the salt component. As the molar ratio of the other examined solvents and the factor affecting surface tension (ST) of the deep eutectic solvents (DESs) increased, the surface tension (ST) of deep eutectic solvents (DESs) constantly dropped.

**4.2. Phase behaviours**

As previously mentioned, two solids capable of self-association are combined to form the deep eutectic solvents (DESs) by forming a new liquid phase by hydrogen bonding [13]. To create deep eutectic solvents (DESs), HBAs (ILs) and HBDs are combined in the proper ratios. Most of the literature now in circulation only takes binary DESs—that is, mixes of one type of hydrogen bond accepter and one type of hydrogen bond donor—into account. The main characteristics of the solid-liquid phase diagrams for these binary deep eutectic solvents (DESs) are summarised in Figure 1(b). The low melting points of the deep eutectic solvents (DESs) in compared to the salts hydrogen bond accepter (HBAs) and hydrogen bond donors (HBDs) that create them are one of the most significant and distinctive known properties of DESs. The formation of strong hydrogen bond accepter (HBA) and hydrogen bond donor (HBD) intermolecular contacts, which are ideal for the eutectic mixture composition, causes melting point lowering during mixing [14] in the case of ChCl + urea, which forms a deep eutectic solvent (DESs) at a 1:2 salt:urea molar ratio. Since interactions between complexes are stronger than those between individual components, eutectic mixtures have a lower freezing point than eutectic components.



**4.3. Freezing point (Tf)**

Table 1 provides a list of the freezing points of various deep eutectic solvents (DESs) mentioned in the literature. It should be emphasised that there are only a few number of deep eutectic solvents (DESs) that are liquid at room temperature, despite the fact that many different amides have been combined with ChCl to create DESs with freezing temperatures below 100 0C. The freezing point of individual parts is lower [15]. The freezing point of a eutectic mixture, for instance, when ChCl and urea are combined in a 1: 2 molar ratio is 12 0C, which is much lower than the MPs of ChCl and urea (302 and 133 0C, respectively). The interaction between the halide anion and the hydrogen bond donor (HBD) component, in this case urea, results in a significant decrease in the freezing point (Tf). Different deep eutectic solvents (DESs) and their components freezing point (Tf) given in table 1.

**4.4. Density**

Applications of the density in process design are widely established. The development of reliable equations of state, which are essential in computing the thermodynamic properties required for the creation of industrial processes, including gas separation techniques, depends on the temperature and pressure effects on density (PVT behaviours). Most well-known deep eutectic solvents (DESs) have densities between 1.0 and 1.35 g cm-3 at 298.15 K, although other DESs that contain metallic salts, as ZnCl2, have densities between 1.3 and 1.6 g cm-3 [16]. A solvent's density is one of its most important physical characteristics. Utilising a specific gravity metre, densities of deep eutectic solvents (DESs) are often determined. The majority of deep eutectic solvents (DESs) have densities greater than those of water. The densities of ZnCl2-HBD eutectic mixtures are greater than 1.3 g cm3. various ZnCl2 compounds have various densities (1.63 g cm3 for ZnCl2-urea and 1.36 g cm3 for ZnCl2-acetamide, respectively). The variable molecular packing (DESs) of the deep eutectic fluids may be responsible for the density discrepancy.

**4.5 Viscosity**

The viscosity of deep eutectic solvents (DESs) is a crucial issue that requires thought. With the exception of the eutectic mixture (EM) of chlor chloride and ethylene glycol (EG), the majority of deep eutectic solvents (DESs) have quite high viscosities (>100 cP) at ambient temperature. The formation of an extensive hydrogen bond network between each component is frequently attributed to the high viscosity of deep eutectic solvents (DESs), which results in a decreased mobility of free species inside the deep eutectic solvents (DESs). The bulk of deep eutectic solvents (DESs) are characterised by large ion sizes and small void volumes, although other forces, including electrostatic or van der Waals interactions, may also be to blame for their high viscosity. The deep eutectic solvents (DESs) components, including the type of ammonium salts and HBDs, the organic salt/HBD molar ratio, and other chemical properties, as well as the temperature and water content, all have an impact on the viscosity of eutectic mixtures. Van der Waals interactions, hydrogen bonds, and electrostatic interactions all have an impact on the viscosity of binary eutectic mixtures. The choice of hydrogen bond donor affects the viscosity of the deep eutectic solvents (DESs) (HBD) based on choline chloride (ChCl).

**4.6 Ionic conductivity**

Due to their relatively high viscosities (lower than 2 mS cm-1 at ambient temperature), the majority of DESs have poor ionic conductivities. The viscosity increases as conductivity decreases. The conductivities of DESs often grow with temperature as a result of a decrease in the DES's viscosity. It is evident that changes in the organic salt/HBD molar ratio have a major impact on DES conductivities because they also significantly affect DES viscosities [17].

Table 1 lists the several deep eutectic's freezing points. [Refs. 7]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Halide salt** | **mp/0C** | **Hydrogen bond donor (HBD)** | **mp/0C** | **Salt: HBD (Molar Ratio)** | **DES Tf/0C** |
|  |  |  |  |  |  |
| ChCl, | 303 | Urea | 134 | 01:02 | 12 |
| ChCl, | 303 | Thiourea | 175 | 01:02 | 69 |
| ChCl, | 303 | 1-methyl urea | 93 | 01:02 | 29 |
| ChCl, | 303 | 1,3-dimethyl urea | 102 | 01:02 | 70 |
| ChCl, | 303 | 1,1- dimethyl urea | 180 | 01:02 | 149 |
| ChCl, | 303 | Acetamide | 80 | 01:02 | 51 |
| ChCl, | 303 | Benzamide | 129 | 01:02 | 92 |
| ChCl, | 303 | Ethylene glycol | -12.9 | 01:02 |  |
| ChCl, | 303 | Glycerol | 17.8 |  |  |
| ChCl, | 303 | Adipic acid | 153 | 01:01 | 85 |
| ChCl, | 303 | Benzoic acid  | 122 | 01:01 | 95 |
| ChCl, | 303 | Citric acid | 149 | 01:01 | 69 |
| ChCl, | 303 | Malonic acid  | 134 | 01:01 | 10 |
| ChCl, | 303 | Oxalic acid  | 190 | 01:01 | 34 |
| ChCl, | 303 | Phenyl acetaic acid | 77 | 01:01 | 25 |
| ChCl, | 303 | Phenyl propionic acid | 48 | 01:01 | 20 |
| ChCl, | 303 | Succinic acid  | 185 | 01:01 | 71 |
| ChCl, | 303 | tricarballylic acid | 159 | 01:01 | 90 |
| ChCl , | 303 | MgCl2 | 116 | 01:01 | 16 |
| ZnCl2, | 293 | Urea | 134 |  | 9 |
| ZnCl2 | 293 | Acetamide | 81 |  | -16 |
| ZnCl2, | 293 | Ethylene glycol | -12.9 |  | -30 |
| ZnCl2, | 293 | hexanediol | 42 |  | -23 |
| Benzyl triphenyl phosphonium chloride | 345-347 | Glycerol | 17.8 |  | 50.36 |
| Benzyl triphenyl phosphonium chloride | 345-347 | Ethylene glycol | -12.9 |  | 47.91 |
| Benzyl triphenyl phosphonium chloride | 345-347 | 2,2,2-trifluoroacetamide  | 73-75 |  | 99.72 |

**4.7 Green credentials**

Deep eutectic solvents (DESs) may oﬀer a “greener” alternative to many traditional ionic liquids (ILs) the unique properties of deep eutectic solvents (DESs) are responsible for widely significant compare to other ionic liquids basis environmental impact, such as a, non-flammability, less toxicity, recyclable, environmentally friendly and biodegradability etc.[18]

**5. Applications of the deep eutectic solvents (DESs)**

For scientists and researchers who conduct ongoing study to comprehend their relevance, the Deep Eutectic Solvents (DESs) are very helpful. Graph 1 shows the statistics for research article publications. Due to their non-toxic, affordable pricing, and recyclable makeup, "Deep eutectic solvents" (DESs) are growing in favour as highly sustainable, distinctive, and environmentally friendly solvents. Ionic liquids (ILs) and deep eutectic solvents (DESs) have excellent qualities and advantages in a number of applications; however, they are not always ecologically benign. In the quest for less toxic and biodegradable materials, a brand-new family of ionic liquids (ILs) has been developed [19]. In order to synthesise polymers, deep eutectic solvents (DESs) have been crucially used in polymer research as solvents, functional additives, and monomers. Below, the potential and applications of deep eutectic solvents (DESs) in material science have been thoroughly addressed.



**Fig: Application of the “deep eutectic solvents” (DESs).**

**The interesting applications of the “deep eutectic solvents” (DESs) are following: -**

1. Metal processing applications
2. Synthesis applications
3. Gas seperation (CO2,SO2)
4. Extraction of catechins from tea
5. Therapeutic applications
6. Extraction and separation
7. Catalyst
8. Agro forestry
9. Biological applications etc.
10. polymer synthesis
11. Synthesis of nanomaterials

**5.1 Metal processing applications**

The integration of metal ions in solutions for metal dissolution or processing, metal deposition, and other uses is most usually accomplished using deep eutectic solvents (DESs). The increased solubility of metal salts in compared to nonaqueous solvents, the absence of water, and the high conductivity are advantages of utilising Deep eutectic solvents (DESs) over aqueous electrolytes [20]. Metal electrodeposition, a variety of electrodeposited coatings with varying features and functionalities, metal electropolishing, processing of metal oxides, and metal extraction are commercialised deep eutectic solvents (DES)-based operations in the metal finishing and metal extraction industries. synthesising metal nanoparticles, etc. [21]

* The copper elctrodeposting is common in surface-finishing industry, and a number of studies involving deep eutectic solvents (DESs) -based copper plating has been done [22- 23].
* Zinc metal deposited Due to corrosion protection capacity; zinc has been importance in metal finishing industry [24].

**5.2 Synthesis applications**

For synthetic processes including biotransformation, biodiesel production, polymer synthesis, and related materials, "Deep eutectic solvents" (DESs) can be employed. Deep eutectic solvents (DESs) are frequently used in polymer synthesis as solvents, functional additives, and monomers. Deep eutectic solvents (DESs) are used in these processes, hence "green" research is needed to ascertain how these processes affect the environment. This is due to the emergence of greener technologies for chemical synthesis. Biocatalysis using the lipase enzyme and deep eutectic solvents (DESs) as a catalyst and recyclable solvent are two "green" ways to carry out the procedure. [25].

**5.2.1 Synthesis of nanomaterials**

Deep eutectic solvents (DESs) have been used as both solvents and reactants to create a variety of nanostructured materials. DES has also been employed as templates, precursors, and dispersants in the manufacturing of nanomaterials to modify nucleation and growth processes, and as designer solvents to change the size and shape of nanomaterials [26].

* Agents of functionalization Deep eutectic solvents (DESs) have also been characterized as functionalization agents, with the bulk of the studies focusing on the functionalization of carbon nanotubes, also known as carbon nanotubes (CNT). As nanoparticles, it is frequently utilised [27].

**5.2.2 Polymer synthesis**

**5.2.2.1 As functional additives**

Deep eutectic solvents (DESs) can also serve as ligand providers and/or templates. Deep eutectic solvents (DESs) have been shown to be suitable as plasticizers for a wide variety of polymeric green compounds. The eutectic mixtures of ChCl:urea and ChCl:glycerol have been used as an additive in the synthesis of cellulose- [28-29] and corn starch- [30] based polymer electrolytes, as well as in the fabrication of agar films.

**5.2.2.2 As solvents**

Deep eutectic solvents (DESs) have been widely used as polymer synthesis solvents. Deep eutectic solvents (DESs) containing choline chloride and urea have been used to make polymers with substantial applications in medicine and industry [31-32].

**5.2.2.3 As monomers**

Deep eutectic solvents (DESs) utilised as a monomer have been documented primarily in two areas: in the creation of polymeric-based “deep eutectic solvents” (DESs) [33- 34] and in the preparation of polymeric-based “deep eutectic solvents” (DESs). as well as in the field of Molecular Imprinted Technology (MIT) The materials created have mostly been used in separation, purification, and extraction technologies.

Liu et al. [35] synthesized magnetic deep eutectic solvents (DESs) used a ChCl: metacrylic acid eutectic mixtures (EMs) as the functional monomer.

**5.3 Gas seperation**

Ionic liquids (ILs) may be replaced with deep eutectic solvents (DESs), which is significant from both an economic and environmental standpoint. A key factor in lowering the greenhouse effect is the capture of carbon dioxide (CO2) and sulphur dioxide (SO2) from gases released by the combustion of fossil fuels in thermal power plants, automobiles, and other sources. The physicochemical properties of deep eutectic solvents (DESs) are therefore responsible for gas separation instruments and studies of gas solubility in deep eutectic solvents (DESs). Because deep eutectic solvents (DESs) have promising characteristics as carbon dioxide (CO2) and sulphur dioxide (SO2) gas separating agents, they may provide a "greener" alternative to many traditional ILs.

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Figure 2. Publication list of deep eutectic solvent [Ref. 12]

**5.4 Extraction of catechins from tea**

Tea is the main source of catechins, which are famous for their high antioxidant potential in humans. Studies on animals and in the lab have connected tea catechins to improved immune function, lower risks for diabetes and obesity, and the prevention of some malignancies. Cardiovascular disease [37]. Deep eutectic solvents (DESs) extractions were compared to ionic liquids (ILs) and conventional solvents because tea catechins are widely used in numerous medications, nutraceuticals, and pretty human health products. Malic acid was present in the DESs, which as hydrogen bond donors demonstrated good solubility of catechins with a range of polarity. the use of the DESs to extract catechins from tea [38]. DESs can be used to extract many kinds of natural elements from biomass in order to produce bioactive chemicals, medications, etc. [39]

**6. Conclusion**

A deep eutectic solvent (DESs) is produced by aggregating a quaternary ammonium salt with hydrogen bond donors (HBDs) or metal salts that can form a complex with the quaternary ammonium salt's halide anion. This review focuses on the preparation of "Deep eutectic solvents (DESs)" and applications of DESs based on their distinctive physicochemical properties. In this part, the physicochemical features of "Deep eutectic solvents" (DESs) will be examined, including studies on their special freezing point, viscosity, surface tension, phase behaviours, conductivity, and pH. Their potential use in material science includes applications for metal processing, synthesis, gas separation (CO2, SO2), tea catechin extraction, therapeutic applications, extraction and separation, catalyst, agroforestry, biological applications, etc. These novel properties of DESs are the cause of their potential use in these applications. The potential usage in material science to enhance the uses of these solvents by expanding the kinds of salts and "hydrogen bond donors" that are used.

**7. Conflict of the interest**

There are no conflicts to declare.

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