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

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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]. Low lattice energy nonsymmetric ions are found in deep eutectic solvents (DESs), 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 (DESs)**

A quaternary ammonium salt can be converted into a deep eutectic solvent (DESs) by combining it with a hydrogen bond donor (HBD) or metal salts that can form a complex with the quaternary ammonium salt's halide anion. Because of charge delocalization caused by hydrogen bonding between the halide ion and subsequently the hydrogen-donor moiety, the combination has a lower freezing point than its individual components do [9]. The substance choline chloride (ChCl) is most frequently used to create deep eutectic solvents (DESs). Easily synthesised from fossil deposits (million metric tonnes) or recovered from biomass, choline chloride (ChCl) is a quaternary ammonium salt [10]. It is reasonably priced, non-toxic, biodegradable, and environmentally safe. A deep eutectic solvent (DES) can be produced 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). Nuclear magnetic resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR) techniques were used to confirm the formation of eutectics and hydrogen bonding in deep eutectic solvents (DESs) [11]. In FTIR spectra and the resonance signal up field of 1H-NMR (protium nuclear magnetic resonance) spectra, changes in the representative peaks and broadening of the implicated bonds can be observed.



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**

Deep eutectic solvents (DESs) are made by combining various hydrogen bond donors (HBD) and various quaternary ammonium salts (QASs), including ChCl. Conductivity, pH, viscosity, surface tension, phase behaviour, and freezing point are some of the physicochemical properties of deep eutectic solvents (DESs). Deep eutectic solvents' physicochemical characteristics will be examined in this section. 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 contains a list of the freezing points for many deep eutectic solvents (DESs) that have been discussed in the literature. It should be noted that there are relatively few deep eutectic solvents (DESs) that are liquid at ambient temperature, despite the fact that several various amides have been combined with ChCl to form DESs with freezing temperatures below 100 0C. The freezing point of distinct components is lower [15]. For instance, when ChCl and urea are mixed in a 1:1 molar ratio, a eutectic mixture is created that has a freezing point of 12 0C, which is much lower than the MPs of ChCl and urea (302 and 133 0C, respectively). The freezing point (Tf) is significantly lowered as a result of the interaction between the halide anion and the hydrogen bond donor (HBD) element, in this case urea. Table 1 lists various deep eutectic solvents (DESs) and their component freezing points (Tf).

**4.4. Density**

Numerous established uses of density exist in process design. The effects of temperature and pressure on density (PVT behaviours) are critical in producing correct equations of state, which are essential in estimating the thermodynamic properties required for the development of industrial processes, including gas separation technologies. The bulk of well-known DESs have densities between 1.0 and 1.35 g cm-3 at 298.15 K, while other DESs that contain metallic salts, like ZnCl2, have densities between 1.3 and 1.6 g cm-3 [16]. The density of a solvent is one of its most important physical characteristics. A specific gravity metre is widely used to determine the densities of deep eutectic solvents (DESs). Densities of deep eutectic solvents (DESs) are often higher than those of water. combinations of ZnCl2 and HBD with densities more than 1.3 g cm3. For example, ZnCl2-acetamide has a density of 1.36 g cm3, while ZnCl2-urea has a density of 1.63 g cm3. The deep eutectic fluids' variable molecular packing (DESs) may be to blame for the variance in density.

**4.5 Viscosity**

The deep eutectic solvents' (DESs) viscosity must be taken into account. At ambient temperature, the majority of deep eutectic solvents (DESs) have quite high viscosities (>100 cP), with the exception of the eutectic mixture (EM) of chlor chloride and ethylene glycol (EG). It is frequently believed that the formation of a dense hydrogen bond network between each component is the cause of the high viscosity of deep eutectic solvents (DESs), which causes a decreased mobility of free species inside the DESs. Deep eutectic solvents (DESs) are characterised by large ion sizes and small void volumes, and their high viscosity may also be a result of electrostatic or van der Waals interactions. The viscosity of eutectic mixtures is influenced by the kind of ammonium salts and HBDs present, their molar ratio with organic salts, other chemical properties, temperature, and water content, among other things. Hydrogen bonds, van der Waals interactions, and electrostatic interactions all have an impact on the viscosity of binary eutectic mixtures. The hydrogen bond donor used determines the viscosity of the choline chloride (ChCl)-based deep eutectic solvents (DESs) (HBD).

**4.6 Ionic conductivity**

Most DESs have weak ionic conductivities due to their relatively high viscosities (lower than 2 mS cm-1 at room temperature). As conductivity declines, viscosity rises. The conductivities of DESs frequently increase with temperature because the viscosity of the DESs decreases. Changes in the organic salt/HBD molar ratio clearly have a large effect on DES conductivities because they also have a considerable impact on DES viscosities [17].

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

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
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| --- | --- | --- | --- | --- | --- |
| **Halide salt** | **mp/0C** | **Hydrogen bond donor (HBD)** | **mp/0C** | **Salt: HBD (Molar Ratio)** | **DES Tf/0C** |
|  |  |  |  |  |  |
| Choline,Chloride (ChCl) | 303 | Urea | 134 | 01:02 | 12 |
| Choline,Chloride (ChCl) | 303 | Thiourea | 175 | 01:02 | 69 |
| Choline,Chloride (ChCl), | 303 | 1-methyl urea | 93 | 01:02 | 29 |
| Choline,Chloride (ChCl) | 303 | 1,3-dimethyl urea | 102 | 01:02 | 70 |
| Choline,Chloride (ChCl) | 303 | Phenyl acetaic acid | 77 | 01:01 | 25 |
| Choline,Chloride (ChCl) | 303 | Phenyl propionic acid | 48 | 01:01 | 20 |
| Choline,Chloride (ChCl) | 303 | Succinic acid  | 185 | 01:01 | 71 |
| Choline,Chloride (ChCl) | 303 | tricarballylic acid | 159 | 01:01 | 90 |
| Choline,Chloride (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 |

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**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)**

The Deep Eutectic Solvents (DESs) are particularly beneficial for scientists and researchers who do continual research to understand its importance. The statistics for research article publishing are displayed in Graph 1. "Deep eutectic solvents" (DESs) are becoming more and more popular as highly sustainable, distinctive, and ecologically friendly solvents due to their non-toxic, reasonably priced, and recyclable makeup. Ionic liquids (ILs) and deep eutectic solvents (DESs) are wonderful materials with many benefits, however they are not necessarily environmentally friendly. A brand-new family of ionic liquids (ILs) has been created in the search for materials that are less hazardous and biodegradable [19]. Deep eutectic solvents (DESs) have been employed extensively in polymer research as solvents, functional additives, and monomers to synthesise polymers. In-depth discussion of the possibilities and uses of deep eutectic solvents (DESs) in material science can be found below,



**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 nanomaterial

**5.1 Metal processing applications**

Deep eutectic solvents (DESs) are most frequently used to integrate metal ions in solutions for metal dissolution or processing, metal deposition, and other purposes. Deep eutectic solvents (DESs) provide advantages over aqueous electrolytes, including greater solubility of metal salts in comparison to nonaqueous solvents, the lack of water, and high conductivity [20]. Deep eutectic solvents (DES)-based commercial operations in the metal finishing and metal extraction industries include metal electrodeposition, a range of electrodeposited coatings with varied characteristics and functions, metal electropolishing, processing of metal oxides, and metal extraction. metal nanoparticle production, 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].
* Metal deposits of zinc Due to its ability to prevent corrosion, zinc has become important in the metal finishing sector [24].

**5.2 Synthesis applications**

"Deep eutectic solvents" (DESs) can be used in a variety of synthetic processes, such as biotransformation, the generation of biodiesel, the synthesis of polymers, and related materials. Deep eutectic solvents (DESs) are frequently employed as solvents, functional additives, and monomers in the production of polymers. Due to the use of deep eutectic solvents (DESs) in these processes, "green" study is required to determine how these procedures harm the environment. This is a result of more

environmentally friendly chemical synthesis processes emerging. Two "green" methods for doing the technique involve employing the lipase enzyme as a catalyst and deep eutectic solvents (DESs) as a recyclable solvent [25].

**5.2.1 Synthesis of nanomaterials**

DESs have been used as both reactants and solvents in a variety of nanostructured materials. In order to change the nucleation and growth processes of nanomaterials, DES has also been utilised in their creation as precursors, dispersants, templates, and designer solvents to change their size and shape [26].

* Functionalizing substances Deep eutectic solvents (DESs) have been characterised as functionalization agents for carbon nanotubes, also known as carbon nanotubes (CNT), while the majority of investigations have focused on the functionalization of CNT. Many people use this material as nanoparticles [27].

**5.2.2 Polymer synthesis**

**5.2.2.1 As functional additives**

DESs, or deep eutectic solvents, can act as ligand suppliers and/or templates. Many different polymeric green compounds have been demonstrated to work well as plasticizers when using deep eutectic solvents (DESs). The production of cellulose- and corn starch-based polymer electrolytes, as well as the creation of agar films, both require the eutectic mixes of ChCl:urea and ChCl:glycerol as an ingredient [28-30].

**5.2.2.2 As solvents**

Solvents for polymer synthesis have frequently used deep eutectic solvents (DESs). Polymers with important uses in industry and medicine have been created using deep eutectic solvents (DESs) that contain choline chloride and urea [31-32].

**5.2.2.3 As monomers**

The development of polymeric-based "deep eutectic solvents" (DESs) and the preparation of polymeric-based "deep eutectic solvents" (DESs) are the two main applications for deep eutectic solvents (DESs) used as a monomer. in the area of Molecular Imprinted Technology (MIT), as well. The majority of the materials produced have been applied to methods for extraction, purification, and separation [33-34].

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**

Deep eutectic solvents (DESs) can replace ionic liquids (ILs), which is relevant from both an economic and environmental perspective. The capture of carbon dioxide (CO2) and sulphur dioxide (SO2) from gases emitted by the combustion of fossil fuels in thermal power plants, vehicles, and other sources is a crucial role in reducing the greenhouse effect. Therefore, research of gas solubility in deep eutectic solvents (DESs) and gas separation equipment are based on the physicochemical features of DESs. Deep eutectic solvents (DESs) may offer a "greener" alternative to many conventional ILs due to their potential as carbon dioxide (CO2) and sulphur dioxide (SO2) gas separating agents.

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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**

Quaternary ammonium salts can be aggregated with metal salts that can form a complex with the quaternary ammonium salt's halide anion or hydrogen bond donors (HBDs) to create deep eutectic solvents (DESs). This article focuses on the creation of "Deep eutectic solvents (DESs)" and the various uses for DESs that are based on their unique physicochemical characteristics. In this section, the physicochemical properties of "Deep eutectic solvents" (DESs) will be investigated, including research on their unique 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.

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