**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 hydrogen bond donor (HBD) or metal salts that can form a complex with the halide anion of a quaternary ammonium salt can be added to the salt to transform it into a deep eutectic solvent (DES). The combination has a lower freezing point than its constituent parts due to charge delocalization brought on by hydrogen bonding between the halide ion and subsequently the hydrogen-donor moiety [9]. The most common ingredient used to make deep eutectic solvents (DESs) is choline chloride (ChCl). As a quaternary ammonium salt, choline chloride (ChCl) is easily synthesised from fossil deposits (million metric tonnes) or recovered from biomass [10]. It's non-toxic, biodegradable, affordable, and safe for the environment. When CHCl aggregates with safe hydrogen bond donors such as urea, renewable carboxylic acids (such as oxalic acid, citric acid, succinic acid, or amino acids), or renewable polyols (such as glycerol, polysaccharides), a deep eutectic solvent (DES) can be generated. To verify the eutectic and hydrogen bonding formation in deep eutectic solvents (DESs), nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) techniques were employed [11]. We can see changes in the representative peaks and broadening of the involved bonds in FTIR spectra and the resonance signal up field of 1H-NMR (protium nuclear magnetic resonance) spectra.



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 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 (HB) 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 HBAs and 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 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)**

Many deep eutectic solvents (DESs) that have been covered in the literature are included in Table 1 as a list of their freezing points. It is worth mentioning that although several other amides have been mixed with ChCl to create DESs with freezing temperatures below 100 0C, the number of DESs that are liquid at normal temperature is still rather small. Distinct constituents have a lower freezing point [15]. For example, mixing urea and ChCl in a 1:1 molar ratio result in a eutectic combination with a freezing point of 12 0C, which is significantly lower than the MPs of urea and ChCl (302 and 133 0C, respectively). The interaction between the halide anion and the hydrogen bond donor (HBD) element—in this case, urea—leads to a considerable decrease in the freezing point (Tf). The component freezing points (Tf) of the different deep eutectic solvents (DESs) are listed in Table 1.

**4.4. Density**

Density is well-established in process design and has several applications. In order to produce accurate equations of state—which are crucial for calculating the thermodynamic properties needed for the development of industrial processes, including gas separation technologies—it is important to include the effects of temperature and pressure on density (PVT behaviours). While some DESs that contain metallic salts, like ZnCl2, have densities between 1.3 and 1.6 g cm-3 at 298.15 K, the majority of well-known DESs have densities between 1.0 and 1.35 g cm-3 [16]. One of a solvent's most significant physical properties is its density. Densities of deep eutectic solvents (DESs) are commonly measured using a specific gravity metre. Deep eutectic solvents (DESs) frequently have densities that are higher than those of water. ZnCl2 and HBD mixtures with densities more than 1.3 g cm3. ZnCl2-acetamide, for instance, has a density of 1.36 g cm3, but ZnCl2-urea has a density of 1.63 g cm3. The density variance could be caused by the variable molecular packing (DESs) in the deep eutectic fluids.

**4.5 Viscosity**

The deep eutectic solvents' (DESs) viscosity ought to be taken into account. At ambient temperature, the general public of deep eutectic solvents (DESs) have quite high viscosities (>100 cP), apart from the eutectic mixture (EM) of choline chloride and ethylene glycol (EG). it is often believed that the formation of a dense hydrogen bond community between every aspect is the purpose of the excessive viscosity of deep eutectic solvents (DESs), which reasons a decreased mobility of free species inside the DESs. Deep eutectic solvents (DESs) are characterized by means of massive ion sizes and small void volumes, and their high viscosity will also be a result of electrostatic or van der Waals interactions. The viscosity of eutectic mixtures is prompted with the aid of the sort of ammonium salts and HBDs gift, their molar ratio with natural salts, different chemical homes, 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 combos. The hydrogen bond donor used determines the viscosity of the choline chloride (ChCl)-based totally deep eutectic solvents (DESs) (HBD).

**4.6 Ionic conductivity**

Since their viscosities are quite high (less than 2 mS cm-1 at ambient temperature), the majority of DESs have poor ionic conductivities. Vessel viscosity increases with decreasing conductivity. Because of the decrease in viscosity, DESs often exhibit increased conductivities with increasing temperature. Given their significant influence on DES viscosities, changes in the organic salt/HBD molar ratio also evidently have a significant impact on DES conductivities [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**

An eco-friendly substitute for numerous conventional ionic liquids (ILs) could be provided by deep eutectic solvents (DESs). Because of their distinct qualities—such as their non-flammability, lower toxicity, recyclable nature, environmental friendliness, and biodegradability—deep eutectic solvents (DESs) have a notably greater environmental impact than other ionic liquids [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**

To make deep eutectic solvents (DESs), quaternary ammonium salts can be combined with metal salts that can form a complex with the halide anion or hydrogen bond donors (HBDs) of the quaternary ammonium salt. The production of "Deep eutectic solvents (DESs)" and the range of applications for DESs that stem from their distinct physicochemical properties are the main topics of this article. The physical and chemical characteristics of "Deep eutectic solvents" (DESs) will be examined in this part. This will include an examination of the DESs' distinct phase behaviours, conductivity, pH, viscosity, and freezing point. 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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