A review on the synthesis of emerging as green designer deep eutectic solvents and potential application in material science

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Abstract

Deep eutectic solvents (DESs) and closely related ionic liquids (ILs) have emerged as green and sustainable solvents due to their low cost, non-toxic nature, and ability to be recycled. DESs are being hailed as viable replacements to traditional organic solvents, with benefits such as reusability, biodegradability, nontoxicity, large-scale availability, low vapour pressure, low flammability, and ease of manufacture. These solvents form when an organic salt (ammonium or phosphonium) combines with a hydrogen-bond donor such as acids, amides, or alcohols (combination of either urea or glycerol with choline chloride). To date, affordable, environmentally friendly, and simple-to-handle solvents are essentially non-existent. As a result, DESs are generating increasing attention in a variety of scientific domains. This review deals with synthesis of DESs and major applications of this new family of solvents DESs.

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

**1. Introduction**

Deep eutectic solvents (DESs) are a type of solvent that is biodegradable, ecologically beneficial, and long-lasting. Deep eutectic solvents (DESs) are a new family of solvents that overcome the expense and toxicity of ionic liquids (ILs) [1-2]. Deep eutectic solvents (DESs) can be made by simply combining two safe components (naturally occurring, inexpensive, renewable, environmentally friendly, and biodegradable components) that can form a eutectic mixture [3-4]. Scientists initially concentrated on the formation of ionic liquids by combining metal salts, primarily aluminium, iron, zinc, tin, and chlorides, with quaternary ammonium salts (QASs). Despite their high melting points, the correct aggregation of both salts results in the creation of a liquid phase eutectic mixture [5-6]. These eutectic mixes are characterised by a significant freezing point dip, usually greater than 150 0C. Chemists may create a vast range of ILs with different physical characteristics, including as freezing point, solubility, viscosity, density, conductivity, physical phenomena, and refractivity, thanks to the ability to chemically change the cationic moiety nearly infinitely with a wide range of anions. DESs have made a name for themselves as a promising solvent.

**2. Definition of DESs**

A deep eutectic solvent (DESs) is generally formed by two or three environmentally friendly and biodegradable components which are capable of aggregation with each other through hydrogen bond interactions, to form a eutectic mixture [7]. Nonsymmetric ions with low lattice energy and hence low melting points, low vapor pressure, high electrical conductivity, thermal stability, good conductivity, non-volatile nature and as well as good thermal stability, are found in deep eutectic solvents (DESs) [8].

**3. Synthesis of deep eutectic solvents**

A deep eutectic solvent (DESs) is obtained by aggregation a quaternary ammonium salt with hydrogen bond donor (HBD) or metal salts that has the ability to form a complex with the halide anion of the quaternary ammonium salt. The reduction in the freezing point of the combination compared to the melting temperatures of the separate components is due to charge delocalization caused by hydrogen bonding between the halide ion and hence the hydrogen-donor moiety [9]. The most widespread chemicals used for the formation of deep eutectic solvents (DESs) is choline chloride (ChCl). choline chloride (ChCl) is a cheap, non-toxic, biodegradable and environmentally friendly quaternary ammonium salt which can be either extracted from biomass or readily synthesized from fossil reserves (million metric tons) through a high atom economy method [10]. In aggregation with safe hydrogen bond donors like urea, renewable carboxylic acids (e.g., oxalic acid, citric acid, succinic acid or amino acids) or renewable polyols (e.g., glycerol, carbohydrates), ChCl is capable of forming a deep eutectic solvent (DESs). The formation of eutectics and hydrogen bonds in deep eutectic solvents (DESs) was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and nuclear magnetic resonance (NMR) techniques [11]. Shifts in the representative peaks and broadening of the involved bonds in the Fourier Transform Infrared Spectroscopy (FTIR) spectra, and the shift in the resonance signal up field in 1H-NMR (protium nuclear magnetic resonance) spectra.

|  |  |
| --- | --- |
| 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 created by combining different quaternary ammonium salts (QASs) (e.g., ChCl) with different hydrogen bond donors (HBD) chemical components in a certain ratio. Deep eutectic solvents (DESs) have a variety of physicochemical features, including freezing point, viscosity, surface tension, phase behaviour, conductivity, and pH. The physicochemical characteristics of Deep eutectic solvents will be examined in this section. In the coming decades, sustainable technologies applied to green-related material science applications should play a key role. Such as in material science, Metal processing applications,Synthesis applications, Gas seperation (CO2,SO2), Extraction of catechins from tea, Therapeutic applications, Extraction and separation, Catalyst, Agro forestry, biological applications etc. play a key role in controlling and reducing the environment pollution. Deep eutectic solvents (DESs) have been proposed as a potential replacement for ionic liquids (ILs) that retain the majority of significant features, such as task-specific character.

**4.1. Surface tension**

Surface tension is a key physiochemical property of deep eutectic solvents (DESs) it is applicable in the field of interface and colloid. The surface tension effect of hydrogen-bonding donors (HBDs) and hydrogen-bonding acceptors (HBAs) on the surface tension was investigated [12]. Furthermore, the surface tension of aggregated systems of deep eutectic solvents (DESs) with other solvents, water, water+ salt (e.g., KCl), acetone, ethanol, ethyl acetate (EtAc) and isopropyl alcohol etc. The presence of crystal water in the salt component of deep eutectic solvents (DESs) would be decrease the surface tension of deep eutectic solvents (DESs). the surface tension of deep eutectic solvents (DESs) decreased continuously with the increase of the molar ratio of other investigated solvents and factor affecting of surface tension of DES show in fig 1 (a).

**4.2. Phase behaviours**

As previously stated, deep eutectic solvents (DESs) are created by combining two solids capable of self-association via hydrogen bonding to produce a new liquid phase [13]. HBAs (ILs) and HBDs in appropriate proportions are mixed to generate deep eutectic solvents (DESs). The majority of the existing literature solely considers binary DESs (i.e., mixtures of one type of hydrogen bond accepter and one type of hydrogen bond donor) Figure 1 (b) summarises the major properties of the solid–liquid phase diagrams for these binary deep eutectic solvents (DESs). One of the most relevant and distinct known properties of deep eutectic solvents (DESs) is their low melting points in comparison to those of the salts hydrogen bond accepter (HBAs) and hydrogen bond donors (HBDs) that form them. In the case of ChCl + urea, which forms a deep eutectic solvent (DESs) at a 1:2 salt:urea molar ratio, the melting point of deep eutectic solvents (DESs) The establishment of strong hydrogen bond accepter (HBA) and hydrogen bond donor (HBD) intermolecular contacts, which are optimum for the eutectic mixture composition, causes melting point lowering during mixing [14]. Decrease the freezing point of eutectic mixture compare to the eutectic components because the resulting of the interaction between complexes. is larger the interaction than individual components.



**4.3. Freezing point (Tf)**

The freezing points of different deep eutectic solvents (DESs) described in the literature are listed in Table 1. Although a variety of amides have been used in conjunction with ChCl to make deep eutectic solvents (DESs) with freezing points below 100 0C, it should be noted that the number of DESs that are liquid at ambient temperature is still limited. Individual components have a lower freezing point [15]. For example, when ChCl and urea are combined in a 1: 2 molar ratio, the eutectic mixture's freezing point is 12 0C, which is significantly lower than that of ChCl and urea (MPs of ChCl and urea are 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**

The density is well-known for process design applications. The construction of acceptable equations of state, which play a crucial role in the computation of thermodynamic characteristics necessary for the development of industrial processes, including gas separation procedures, is dependent on the temperature and pressure effects on density (PVT behaviours). Most regarded deep eutectic solvents (DESs) have density in the 1.0–1.35 g cm–3 range at 298.15 K, however certain deep eutectic solvents (DESs) containing metallic salts such as ZnCl2 have densities in the 1.3–1.6 g cm–3 range [16]. The density of a solvent is one of its most essential physical qualities. Densities of deep eutectic solvents (DESs) are usually measured using a specific gravity metre. The densities of most deep eutectic solvents (DESs) are higher than those of water. ZnCl2–HBD eutectic combinations have densities more than 1.3 g cm3. ZnCl2–urea (1: 3.5) and ZnCl2–acetamide (1: 4) have different densities (1.63 and 1.36 g cm3, respectively). The difference in density might be related to the deep eutectic fluids' different molecular arrangement or packing (DESs).

**4.5 Viscosity**

The viscosity of deep eutectic solvents (DESs) is a critical subject that requires attention. Except for the eutectic mixture (EM) of ChCl and ethylene glycol (EG), most deep eutectic solvents (DESs) have relatively high viscosities (>100 cP) at ambient temperature. The development of an extensive hydrogen bond network between each component is typically attributed to the high viscosity of deep eutectic solvents (DESs), which results in a decreased mobility of free species within the deep eutectic solvents (DESs). Most deep eutectic solvents (DESs) have large ion sizes and tiny void volumes, but additional forces such as electrostatic or van der Waals interactions may also contribute to their high viscosity (DESs). The chemical composition of the deep eutectic solvents (DESs) components (type of ammonium salts and HBDs, organic salt/HBD molar ratio, etc.), the temperature, and the water content all influence the viscosity of eutectic mixtures. Hydrogen bonds, van der Waals interactions, and electrostatic interactions all have a role in the viscosity of binary eutectic mixtures. The type of the hydrogen bond donor influences the viscosity of 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). The lower the conductivity, the higher the viscosity. The conductivities of DESs usually increase as the temperature rises due to a reduction in the viscosity of the DES. Given that variations in the organic salt/HBD molar ratio have a significant influence on DES viscosities, it is obvious that this parameter has a significant impact on DES conductivities [17].

Table 1. freezing points of various deep eutectic. [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 |
| Methyl triphenyl phosphonium bromide | 231-233 | Glycerol | 17.8 |  | -4.03 |
| Methyl triphenyl phosphonium bromide | 231-233 | Ethylene glycol | -12.9 |  | -49.34 |
| Methyl triphenyl phosphonium bromide | 231-233 | 2,2,2-trifluoroacetamide | 73-75 |  | -69.29 |

**4.7 Green credentials**

DESs may oﬀer a “greener” alternative to many traditional 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.

Table 2. The physical properties of Deep eutectic solvents (DESs), ionic liquids (ILs) and molecular solvents at 298K.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **SALT (mol equiv)** | **HBD (mol equiv)** | **VISCOCITY /cP** | **CONDUCTIVITY mS cm-1** | **DENSITY / gcm-3** | **SURFACE TENSION**  |
| **/mNm-1**  |
| ChCl (1) | Urea (2) | 632 | 0.75 | 1.24 | 52 |
| ChCl (1) | ethylene glycol (2) | 36 | 7.61 | 1.12 | 49 |
| ChCl (1) | glycerol (2) | 376 | 1.05 | 1.18 | 55.8 |
| ChCl (1) | Malonic acid (1) | 721 | 0.55 |  | 65.7 |
| C4mimCl | AlCl3 | 19 | 9.2 | 1.33 |  |
| ChCl (1) | CrCl3.6H2O | 2346 | 0.37 |  | 77.3 |
| C4mimBF4 | - | 115 | 3.5 | 1.14 | 46.6 |
| C4mim (CF3 CO2)2N | - | 69 | 3.9 | 1.43 | 37.5 |
|  | ethanol | 1.04 |  | 0.785 | 22.39 |

**5. Applications of the deep eutectic solvents**

Deep eutectic solvents (DESs) are very applicable scientist and researchers doing research continuously to know about the importance of deep eutectic solvents (DESs). The numbers of research paper publication shown in graph 1. Deep eutectic solvents (DESs) are emerging as highly environmentally friendly, [18] novel and sustainable solvents deep eutectic solvents (DESs) non- toxic, inexpensive, and recyclable nature of the deep eutectic solvents (DESs). The marvellous properties and advantages in wide range of applications of deep eutectic solvents (DESs), ionic liquids (ILs) are not intrinsically green. In a search for less toxicity and biodegradable, a new type of ionic liquids (ILs) has been developed [19]Significantly deep eutectic solvents (DESs) in polymer science as synthesis of polymer deep eutectic solvents (DESs) have been fundamentally used in polymer science as solvents, functional additives and monomers. The potential and material science applications of deep eutectic solvents (DESs) have been widely explored below.

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

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

**5.1 Metal processing applications**

The integration of metal ions in solution for metal dissoultion or metal processing, metal deposition, and other uses for Deep eutectic solvents (DESs) are the most common. When compared to nonaqueous solvents, the advantages of employing Deep eutectic solvents (DESs) over aqueous electrolytes include the high solubility of metal salts, the lack of water, and the high conductivity [20]. Metal electrodeposition, a range of electrodeposited coatings with various characteristics and functions, metal electropolishing, processing of metal oxides, and metal extraction are all commercialised DES-based processes in the metal finishing and metal extraction sectors. Synthesis of 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**

Deep eutectic solvents (DESs) are applicable for synthetic applications such as biotransformation, purifying and manufacturing biodiesel synthesis of polymers and related materials. synthesis of polymer, deep eutectic solvents (DESs) have been fundamentally used in polymer science as solvents, functional additives and monomer. The adoption of greener methodologies in chemical synthesis, the “green” research to need the develop the environmental implications of doing these synthetic methods with deep eutectic solvents (DESs). Biocatalysis using the enzyme lipase and Deep eutectic solvents (DESs) as a catalyst and recyclable solvent are two "green" techniques for the process [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 characterised 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**

Deep eutectic solvents (DESs) have lately been proposed as a possible replacement for ionic liquids (ILs) that is most important economically and environmental viewpoints. Carbon dioxide (CO2), sulfur dioxide (SO2), captures from emitted gases by burning of fossil fuels in thermal power plants, automobile etc., it is playing a pivotal role to reducing the greenhouse effect. Therefore, because of the promising characteristics of Deep eutectic solvents (DESs) as carbon dioxide (CO2) and sulphur dioxide (SO2) gas separating agents, the physicochemical properties of Deep eutectic solvents (DESs) are responsible for gas separation instruments and on the studies of gas solubility in Deep eutectic solvents (DESs) [36] DESs may oﬀer a “greener” alternative to many traditional ILs the exclusive 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.

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

**5.4 Extraction of catechins from tea**

Most significantly source of catechin is a tea, they become well known for their Numerous humans, antioxidant potential. animal, and in vitro studies its linked tea catechins with prevention of a types of cancers, reduction of the risks for diabetes, obesity, and improvement of the immune system.[37] and cardiovascular disease. Tea catechins are widely used in various pharmaceuticals, nutraceuticals, and pretty human health, Deep eutectic solvents (DESs) extractions were compared to ionic liquids (ILs) and conventional solvent. Deep eutectic solvents (DESs) contained malic acid, as hydrogen bond donors showed a good solubility of catechins with by different polarities. the extraction of catechins from tea by the help of Deep eutectic solvents (DESs) [38]. DESs is also applicable for extraction of different types of natural components from the biomass extraction of bioactive compounds or drugs etc. [39]

**6. Conclusion**

This review is focused the preparation of deep eutectic solvents (DESs), and application of deep eutectic solvents (DESs) basis their unique physicochemical properties of deep eutectic solvents (DESs), a deep eutectic solvent (DESs) is obtained by aggregation a quaternary ammonium salt with hydrogen bond donor (HBD) or metal salts that has the ability to form a complex with the halide anion of the quaternary ammonium salt. Studies on deep eutectic solvent (DESs) unique physicochemical properties such as freezing point, viscosity, surface tension, phase behaviours, conductivity, and pH in this section will be discussed the physicochemical properties of Deep eutectic solvents (DESs). This novel properties of DESs are responsible for their potential application in material science is like metal processing applications, synthesis applications, Gas seperation (CO2, SO2), extraction of catechins from tea, Therapeutic Applications, Extraction and Separation, Catalyst, Agro forestry, biological applications etc. The potential application in material science to expanded the types of salts and hydrogen bond donors which are used and hence further increase the applications of these solvents.

**7. Conflict of interest**

There are no conflicts to declare.

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