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Green Approach in Organic Synthesis

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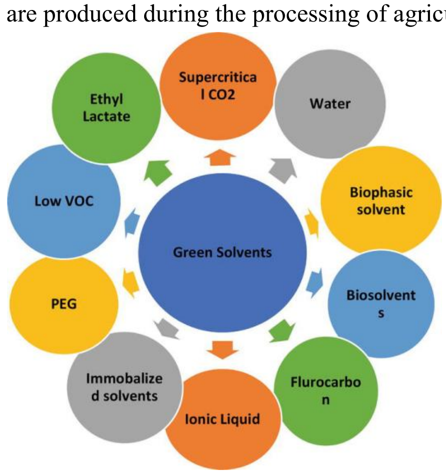
Abstract: *Solvents are liquid compounds that, when applied, dissolve other chemicals, which can be retrieved unmodified once the solvent is removed. The notion of green solvents refers to the goal of reducing the environmental impact of solvents used in chemical synthesis. Green solvents are low-toxicity solvents that are biocompatible with the environment and less harmful than conventional organic solvents. Green solvents are those that are safe for both the environment and humans. Traditional solvents can be replaced with green solvents as a long-term solution to reduce and mitigate environmental degradation. In organic synthesis, green solvents include ionic liquids and deep eutectic mixtures. The review concentrates on the properties, applications, and limitations of various solvents*

Keywords: Solvents

I. INTRODUCTION

1.1. Green solvents

What are green solvents? Green solvents, often known as ecologically friendly solvents, are results of crop processing. In 2015, the United Nations adopted a new development strategy that prioritized sustainability and was based on 17 Sustainable Development Goals. The article emphasizes the importance of "green chemistry" and "green solvent" for future ecologically friendly chemistry (see Figure 1). So-called green, ecological, biodegradable, and sustainable solvents have emerged in this setting [1], which were developed as a less hazardous alternative to petrochemical solvents known as biosolvents, which are produced during the processing of agricultural crops.



Types of green solvent

1.2. Ionic liquid

The phrase "ionic liquid" refers to a family of non-molecular substances with melting temperatures less than 100°C that are composed entirely of ions. ILs offers various advantages over typical organic solvents. ILs has minimal vapor pressure at room temperature and are highly thermally stable, making them good solvents for a variety of extraction

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procedures. The physical and chemical properties of ILs can be altered by simply changing the combination of cations and anions, such as viscosity, thermal stability, and solubility in water and other organic solvents.

Over the last two decades, ILs have emerged as a promising family of solvents with distinct features that have found uses in organic synthesis, electrochemistry, catalysis, metal separation, gas separation, energy storage devices, biomass processing, medicines, and tribology. Ionic liquids are also known by several names, including neoteric solvents, designer solvents, ionic fluids, and molten salts.

In 1914, the first room temperature ionic liquid [EtNH3][NO3] (m.p. 12°C) was discovered [1]. Whether a functional group is connected to the cation and/or anion. Ionic liquid for anhydrous reaction conditions. It has been observed that ionic liquids [C4C1im][HSO4] and [C4C1im][MeSO3] may be successfully employed for lignocellulosic biomass treatment even in the presence of considerable amounts of water; thus, the use of ILs eliminates the need for anhydrous conditions during pretreatment [2]. Acidic ionic liquids have been successfully used to saccharify cellulose and turn it into important compounds such as hydroxymethylfurfural, levulinic acid, and furfural [3, 4, 5, 6, 7, 8, and 9].

1.2.1 Ionic liquid as organocatalyst

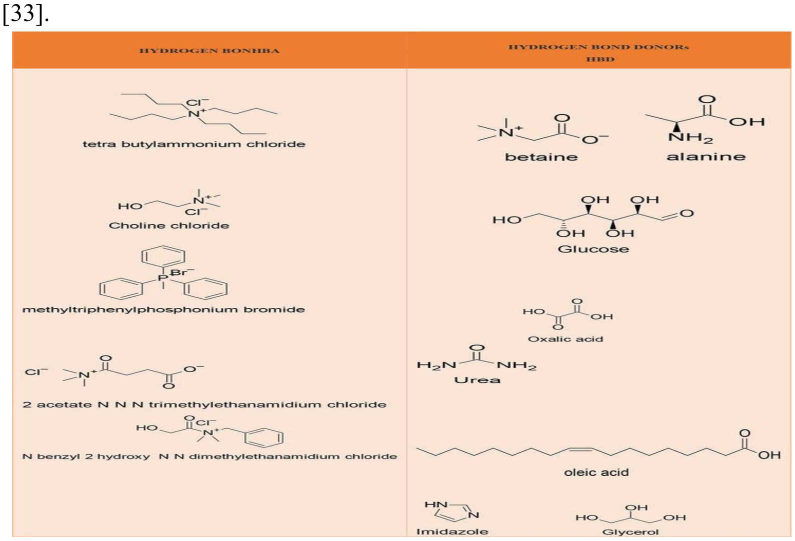
Sulfur functionalized chiral ionic liquid was synthesized as an organocatalyst and utilized to prepare trans epoxide with high diastereo selectivity and enantio selectivity up to 72% ee from different aromatic aldehydes using benzyl bromide in aqueous conditions.

1.2.2 ILs as support for catalyst/reagents

The importance of ionic liquids as soluble supports for catalyst/reagent immobilization [10] has been well studied in various ionic liquid supported synthesis (ILSS) and is applied for a number of organic reactions such as the Knoevengeal reaction [11], 1,3-cycloadditions [12], oligosaccharide synthesis [13], Suzuki coupling [14], synthesis of thiazolidinones [15], and Grieco's multi component synthesis of tetrahydroquinolines [16]. All of the documented responses are attributable to the regulated solubility and nonvolatility of ILs. Common ILs have several limitations, including high toxicity, non-biodegradability, complex production requiring purification, and expensive starting material costs [17–32].

1.3 Deep Eutectice Solvents (DESs)

Deep Eutectic Solvents (DESs) are non-ideal mixtures of two biodegradable ingredients (HBA and HBD) (Table 1) that exhibit strong hydrogen bonding interactions. They are also known in the literature as Deep Eutectic Ionic Liquids (DEILs), Low Melting Mixtures (LMMs), Natural Deep Eutectic Solvents (NADES), and Low Transition Temperature Mixtures (LTTMs). [33].



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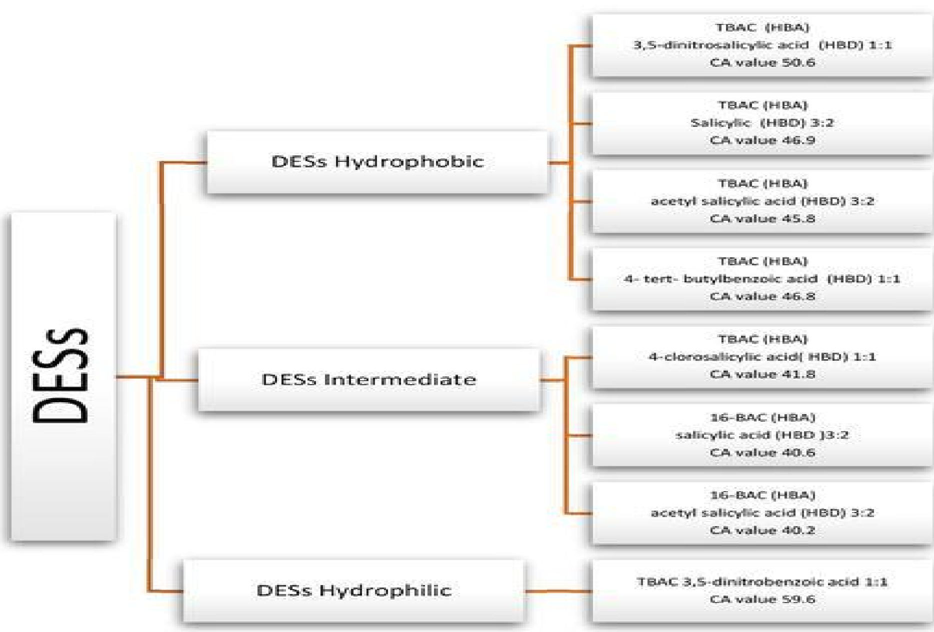
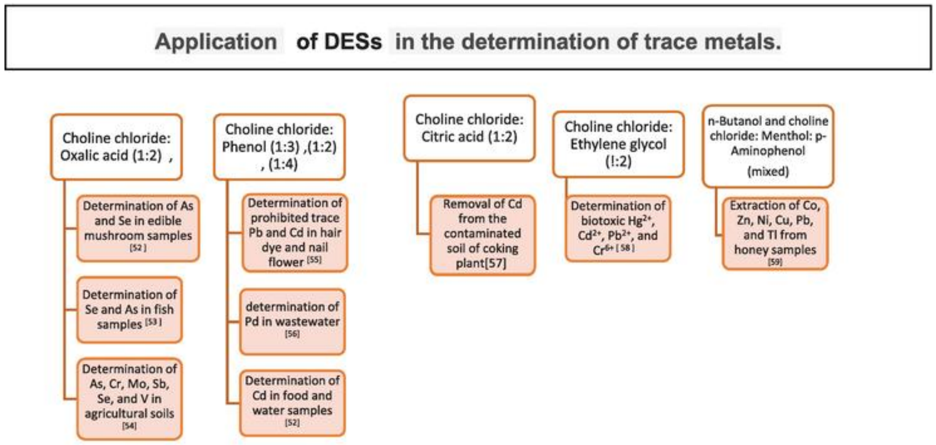
Deep Eutectic Solvent (DES) refers to a very non-ideal mixture of two biodegradable ingredients (HBA and HBD) with significant hydrogen bonding interactions. Many DESs have been produced and used as solvents in chemical processes, dye extraction, protein extraction, nucleic acid extraction, metal separation, and more [34, 35, 36, 37, 38]. Abbott et al. [39] introduced the term "Deep Eutectic Solvent" to describe the formation of a liquid eutectic mixture (melting point 12°C) from two solid materials with high melting points: (i) choline chloride (ChCl), (2-hydroxyethyl)trimethylammonium chloride (melting point 133°C), and (ii) urea (melting point 302°C) in a ratio of 1:2 (1ChCl2Urea) [40, 41].

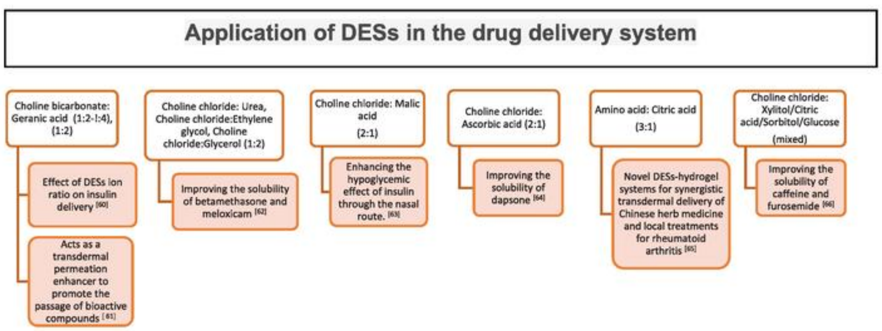
Cichocki et al. established a method to determine the polarity and hydrophobicity of DESs [42]. This technique avoids the need for solution preparation, preserving the internal structure of DESs. The presence of an additional component, like as water or another solvent, can alter the DES molecule's hydrogen bonding process. The contact angle test is one method for determining DES hydrophobicity without having to prepare the solutions. The approach requires no solvents, just an optical goniometer and a reference surface. To define DES characteristics as hydrophobic or hydrophilic, contact angle values measured on glass were compared to highly hydrophobic rapeseed oil and very hydrophilic water, which served as reference substances. DES molecules with contact angle values that were between those of water and oil were classified as having intermediate characteristics. The contact angle thus indirectly quantifies the proximity of DES molecules to the surface of the reference substance. Figure 2 summarizes the contact angle measurement results.

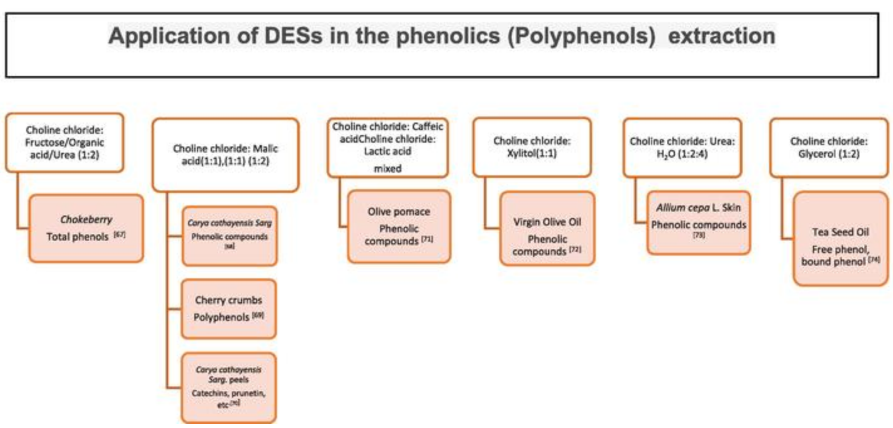


Types of Deep Eutectic Solvent (DES)

Type I DES	Quaternary ammonium salt and metal chloride. Imidazolium salts and various metal halides such as $ZnCl_2$, $FeCl_2$, AgCl, $CuCl_2$, $CdCl_2$, LiCl, $SnCl_2$, and $SnCl_4$
Type II DES	Quaternary ammonium salt and hydrate of metal chloride hydrate
Type III DES	Quaternary ammonium salt as HBA and HBD. Mainly composed of choline chloride and HBDs (carboxylic acids, alcohols, amides, and carbohydrates, etc.)
Type IV DES	Metal chloride (particularly transition metal chloride) and HBD
Type V DES	New class mixture of non-ionic molecular HBA and HBD







II. CONCLUSION

With increased awareness of environmental hazards, researchers are focusing their efforts on replacing poisonous and damaging elements with less harmful constituents. In this direction, ionic liquids (ILs) and deep eutectic liquids (DES) have found numerous effective synthetic applications in a variety of disciplines of study. DESs have a wide range of applications, including metal processing, trace metal extraction, drug delivery, polyphenol and flavonoid extraction, chemical synthesis, biotransformations, and biomedical applications. DES was used as a solvent or cosolvent in a variety of processes due to its strong solubility or miscibility with the substituents. As a result, DESs as acid catalysts can easily be used as a replacement to conventional catalysts. One of the most promising aspects of using DES as a catalyst in diverse chemical syntheses is its reusability or recycling. Flavonoids and phenolic components offer a wide spectrum of pharmacological and therapeutic properties, so extracting flavonoids and polyphenols has long been a research hotspot, with the use of DES replacing harmful organic solvents. Because the majority of the components that comprise DESs are natural products, they can be easily transformed into many types of organisms in nature. DES may operate as both a solvent and a catalyst; this dual capability of biodegradable, greener solvents will pave the way for organic synthesis in the future. Further research on DES for detecting and extracting NTs is required to fully understand the potential of DESs, which could have substantial implications for the diagnosis and treatment of neurological illnesses, as well as to optimize their use for practical applications. This book chapter provides a brief overview of some of the most recent ILS and DES applications in various fields.

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