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Cellulose Dissolution for Edible Biocomposites in Deep Eutectic Solvents: A Review

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Abstract

Organic solvents are vital in chemical synthesis, storage, and separation processes. However, the widespread use of these solvents in industries and research laboratories raises concerns regarding their high volatility, lipophilicity, and toxicity, which pose significant risks to the surroundings and human well-being. In light of these issues, Deep eutectic solvents which is known as a green solvent have become a promising substitute with the potential to alleviate these concerns. DESs have shown remarkable progress in production and manufacturing across various fields. Extensive work investigated the dissolution of renewable materials, mainly cellulose, in multiple solvents, thereby bringing DESs to the forefront of scientific inquiry. These DESs have greatly improved production and manufacturing processes in diverse industries. However, it is important to note that DESs have considerably lower levels of cellulose solubility for edible biocomposites. Cellulose derived from edible fibers finds extensive applications in food and beverage, agriculture, cosmetics, textiles, medical and pharmaceutical industries, agro-industries, and furniture industries. This review includes a comparative analysis of various DES-based solvents, which addresses concern pertaining to the toxicity of DESs, outlines essential properties to consider when selecting DESs for diverse applications, and highlights recent advancements in the fields of extraction media, biofilm production, nanomaterial synthesis, composite material manufacturing, and plasticizer applications.

Abbreviations

HPMC: Hydroxypropyl methylcellulose, MCC: Microcrystalline cellulose, MTU: Methyl thiourea, DES: Deep eutectic solvent, NMMO: N-methyl morpholine-N-oxide, CNF: Cellulose nanofibrils, XRD: X-ray diffraction, 1H NMR: Proton nuclear magnetic resonance spectroscopy, FTIR: Fourier transform infrared spectroscopy, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, DSC: Different scanning calorimetry, TGA: Thermogravimetric analysis, POM: Polarized optical microscopy, HDES: Hydrophobic deep eutectic solvents, MIP: Molecularly imprinted polymer, MDES: Magnetic Deep Eutectic Solvents, PVOH: Polyvinyl alcohol, HBA: Hydrogen bond acceptor, HBD: Hydrogen bond donor, NADES: Natural deep eutectic solvent

Keywords: Cellulose; Nano-cellulose; Edible biocomposites; Dissolution; Deep eutectic solvents

1. Introduction

In light of growing concerns about industrialization, significant efforts are being dedicated to developing solvent systems capable of dissolving renewable cellulose. Various solvents have emerged successfully, enhancing the dispersion and dissolution of cellulose. Notably, ionic liquid solvents (ILs) have developed as highly effective methods for dissolving cellulose (Peng et al., 2022; Prabhune et al., 2023), exhibiting efficient dissolution properties across different temperatures without causing structural distortion (Hawkins et al., 2021; Ries et al., 2018). Despite the widespread use of these ILs, there is a current need for their expansion due to their toxic effects. Shao et al. (2020) have indicated that these solvents can cause DNA damage and increased progeny malformations due to prolonged exposure. Furthermore, the application of ionic liquids has been associated with the discoloration of chlorophyll in plants (Chu et al., 2022), and the high cost of removing toxic substances from ionic solvents is also a limiting factor in their production or synthesis (Sulthan et al., 2023). Hence, utilizing a suitable solvent in the process industry is imperative.

Studying natural deep eutectic solvents (NADES) and DES has generated significant interest as viable options for cellulose dissolution. NADES consist of naturally derived components, including a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) (Nguyen et al., 2020). On the other hand, DES is composed of low lattice energies with large non-symmetric ions and melting temperatures (Prabhune & Dey, 2023). A typical DES formulation follows the structure $Cat^{+}\,{}^{-}X_{z}Y$, where Cat^{+} commonly represents PH_4^{+}, NH_4^{+}, or SR_3^{+}, and X represents a Lewis base, typically a halide. DES offers advantages similar to ionic liquid solvents (ILS) (Wang et al., 2020). However, DES preparation is considerably more accessible and cost-effective, involving mixing natural and readily available components (Lomba et al., 2021). Compared to ILS, DES exhibits lower toxicity levels and is highly biodegradable, making it more environmentally friendly (Suthar et al., 2023). In the study conducted by Chen & Mu et al. (2021), a thorough examination was undertaken to elucidate thirteen distinct strategies associated with DESs, some of which do not align with eco-friendly principles. These strategies entail the utilization of biodegradable and naturally abundant raw materials, the implementation of stepwise synthesis procedures, and the incorporation of specific functional groups to mitigate the toxicity inherent in ILs and DESs. Consequently, microorganisms, such as bacteria or yeast, frequently serve as preferred test organisms in toxicity assessments due to their heightened sensitivity to environmental alterations, including exposure to hazardous substances (Torregrosa-Crespo et al., 2020).

There is lower toxicity of DES, and it has superior environmental quality compared to ILS (Prabhune & Dey, 2023; Sulthan et al., 2023). The toxicity study of DES is not widely explored which can be evaluated using various techniques, including the assessment of cell viability through colorimetric measurements, the luminescence inhibition microtox assay, drop plate methods, and a biological assay based on Fourier-transform infrared spectroscopy (FTIR) (Marchel et al., 2022). The lower toxicity of DES is attributed to its components being derived from nature, and the preparation of DES involves a simple ratio, unlike the synthetic approach used in ILS. Also, the analysis conducted by Omar & Sadeghi (2022), which evaluated the chloride-based HBA in DES with different HBD compounds in binary solution at 25^{o}C producing a viscous solution from 36-8500cps and density is higher than water. Meanwhile, the toxicity depends on the HBA and HBD chemical structures in the DES mixture and demonstrates a non-toxic and biodegradability towards substances.

The growing concern over environmental issues, climate pattern changes, and global warming sparked significant interest in producing green composites based on biopolymers and reinforcing natural fibers such as cellulose. Consequently, a considerable focus has been on utilizing eco-friendly bio-based materials and developing edible biocomposites. These include exploring the conversion of agricultural waste into feed (Bayram et al., 2021; Valdés et al., 2014). One area of exploration involves the utilization of cellulose material such as corn husks in various applications, such as bioplastics, nanocomposites, flame-resistant wood plastic materials, composite polymers, and paper production. Recent research, Ratna et al. (2022), has delved into the dissolution of these fibers, expanding their potential and broadening the range of applications in which they can be effectively employed. When natural fibers are reinforced with biopolymers, they form green composites. K-carrageenan is an example of a polysaccharide biopolymer derived from seaweed, which can be used in biocomposite complexes for bioplastic, oral dispersible film and hard capsule production in the incorporation of cellulose (Mat Yasin et al., 2022; Sapiee et al., 2023, Ramli et al., 2023). K-carrageenan has been reinforced with cellulose at the micro and nanoscales to form an edible polymer.

Edible biocomposites consist of cellulose, which is classified as a natural fiber (Bakar et al., 2023). Natural fibers encompass vegetables, animals, and mineral fibers. Vegetable fibers include leafy materials from fruits and vegetables like pineapple and banana, bast-based materials from kenaf, jute, and flax, and seed-based materials such as coir, cotton, and rice husk (Ratna et al., 2022). These edible fibers comprise holocellulose, lignin, cellulose, and hemicellulose, along with small proportions of ash, proteins, starch, and sugars (Fatima Haq et al., 2022; Hamdan et al., 2021). The dissolution of cellulose from these fibers finds extensive use in various industrial processes today. Lignocellulosic biomass has attracted considerable attention as a promising reservoir owing to its ample and sustainable characteristics. This category of biomass manifests intricates and robust architectures predominantly encompassing cellulose, hemicellulose, and lignin. These inherent structural traits substantially contribute to the intrinsic resistance of biomass, consequently bestowing a sustained complexity upon the endeavor to efficiently convert and meticulously scrutinize biomass (Wang et al., 2023). Notably, cellulose dissolution has been effectively demonstrated by utilizing diverse solvents such as ionic liquids. However, within the scope of this comprehensive review, our focus predominantly centers on the dissolution of this edible biocomposite using DES. This choice is driven by the lower toxicity and facile preparatory attributes of DES, imparting heightened viability to the dissolution process.

However, cellulose derived from these edible biopolymers is not readily soluble (Wang et al., 2020). These are primarily due to forming an intermolecular solid or intramolecular hydrogen bonding network, as illustrated in Figure 1. Consequently, there is a pressing need for safe solvents like DES, which an disrupt the cellulose structure by altering the hydrogen interaction within the cellulose. The dissolution of cellulose has attracted numerous researchers who are actively investigating ways to achieve complete cellulose dissolution using DES solvents. A suitable HBD and HBA in the solvent structure must be able to break the cellulose hydrogen bonding network. In a strong hydrogen bonding interaction between a substance that can donate hydrogen bonds and the negatively charged part (anion) of a substance that accepts hydrogen bonds. This resulted in the anion appearing larger than its actual size due to the hydrogen bond network. This effect is beneficial for the dissolution of cellulose because the larger anion size weakens the interactions between the anion and the positively charged components around the cellulose molecules. As a result, the bonds that hold cellulose together are weakened, facilitating its dissolution process (Omar & Sadeghi, 2023).

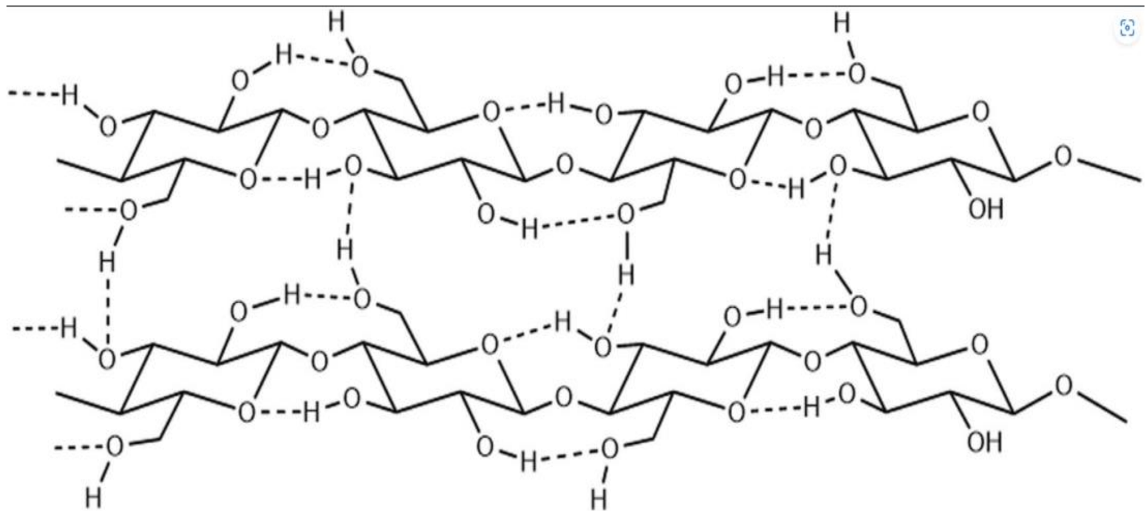

Figure 1. Molecular structures of cellulose with complex hydrogen networking consist of hydrogen bond donor and acceptor (Lin & Tsuchii, 2022).

As industrial processes move towards greener solutions, research on DES has been conducted to optimize their use as solvents. On the other hand, the most commonly used form of cellulose is microcrystalline cellulose (MCC), derived from plant fibers and consists of observable cellulose particles under a microscope (Bubeník et al., 2023). MCC has been incorporated into the matrix of edible biocomposites, resulting in improved tensile strength of the films, reduced water content, enhanced overall appearance, and improved material properties, thereby facilitating cellulose dissolution (Othman et al., 2021). For effective dissolution of this cellulose, the DES component must possess good hydrogen bond accepting and donating abilities (Fu et al., 2020). This paper review aims to evaluate the success of cellulose dissolution in solvents and identify environmentally friendly solvents that are safe for consuming edible biocomposites.

2. Deep Eutectic Solvents and It's Preparation

When DES is combined in the appropriate stoichiometric ratio, it consists of a minimum of two solid or liquid components, forming a stable, homogeneous, and liquid phase (Abranches & Coutinho, 2022). These solvents were introduced in the early 20th century as a novel and environmentally friendly alternative, addressing the growing concerns surrounding the usage of highly poisonous and risky chemicals within the environment (Abbott et al., 2004; Prabhune & Dey, 2023). Figure 2 illustrates various HBAs and HBDs and typical examples of DES molecules and their types.

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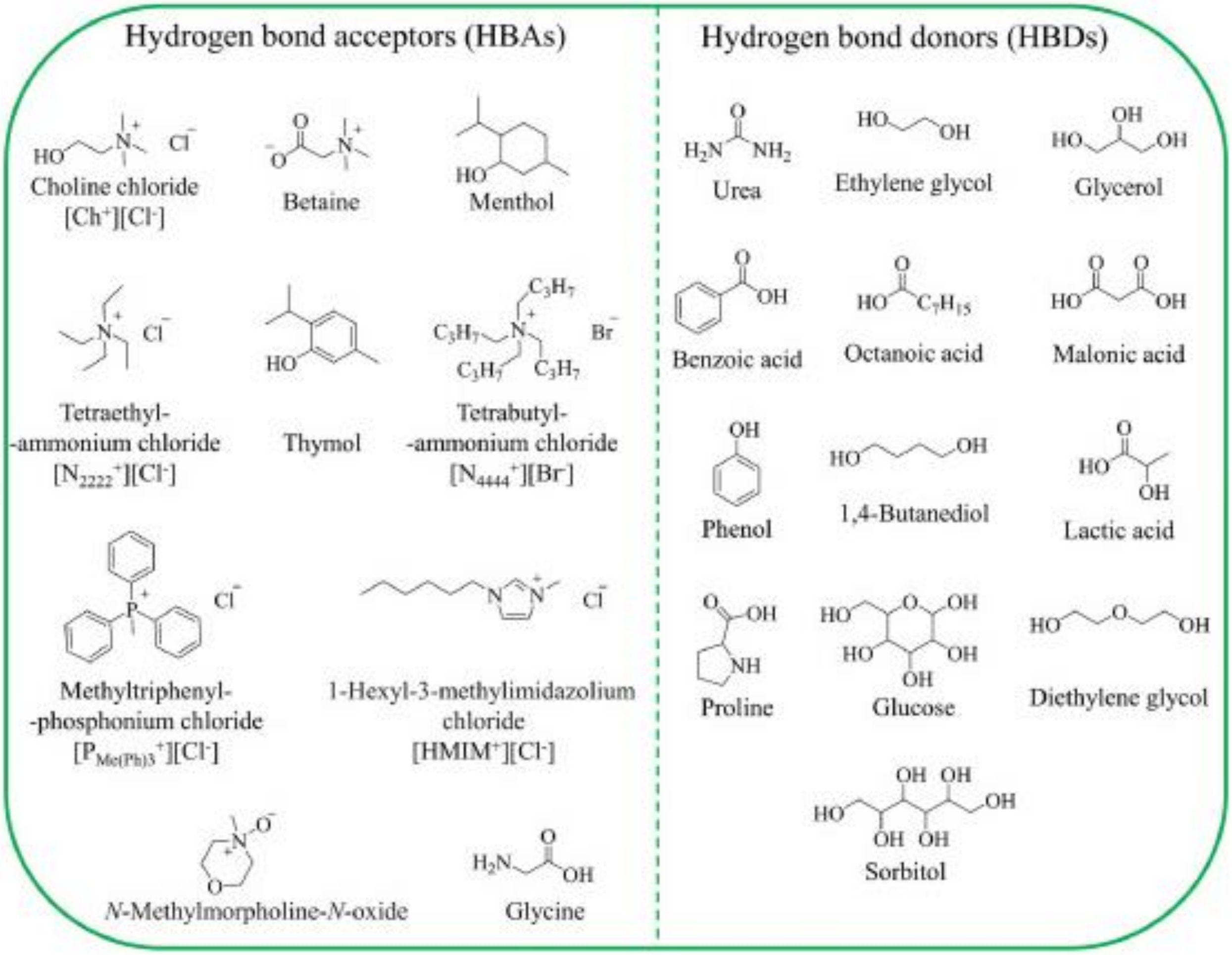
Hydrogen bond acceptors (HBAs)
Hydrogen bond donors (HBDs)
Choline chloride
[Ch+][Cl-]
Betaine
Menthol
Tetraethyl-
-ammonium chloride
[N2222+][Cl-]
Thymol
Tetrabutyl-
-ammonium chloride
[N4444+][Br-]
Methyltriphenyl-
-phosphonium chloride
[PMe(Ph)3+][Cl-]
1-Hexyl-3-methylimidazolium
chloride
[HMIM+][Cl-]
N-Methylmorpholine-N-oxide
Glycine
Urea
Ethylene glycol
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Glucose
Diethylene glycol
Sorbitol

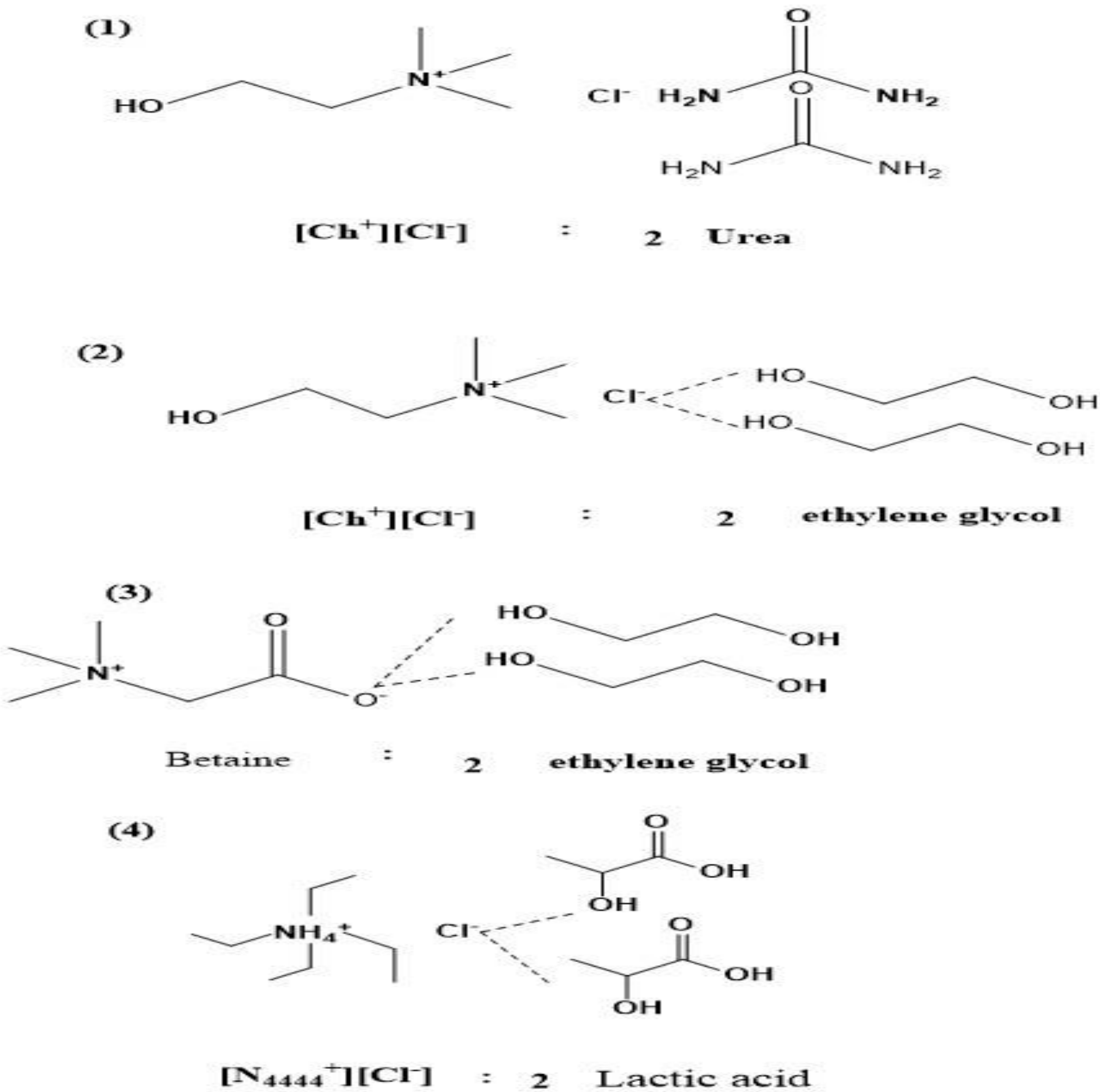

Figure 2: HBAs and HBDs with Common DES (Farooq et al., 2020)

DESs are produced by heating or combining HBAs and HBDs in a simple ratio (Abbott et al., 2003; Bashir et al., 2023). DES has low melting temperatures when compared to their individual HBA or HBD components as a result of the decentralization of the electric charge produced by hydrogen bonding (Sulthan et al., 2023). Quaternary ammonium salts (Shishov et al., 2022), amino acids (Ahmad et al., 2022), and zwitterions (Sharma et al., 2021) are commonly used examples of

HBAs. On the other hand, common HBDs include urea, sugars, carboxylic acids, and polyols (Tiecco et al., 2022). These readily available and cost-effective HBAs and HBDs provide the flexibility to adjust the characteristics of DESs, including viscosity, density, melting point, and refractive index, by varying their types (Saikia & Bhattacharyya, 2023). Therefore, selecting HBAs and HBDs is crucial in developing a safe dissolution process for edible biocomposites.

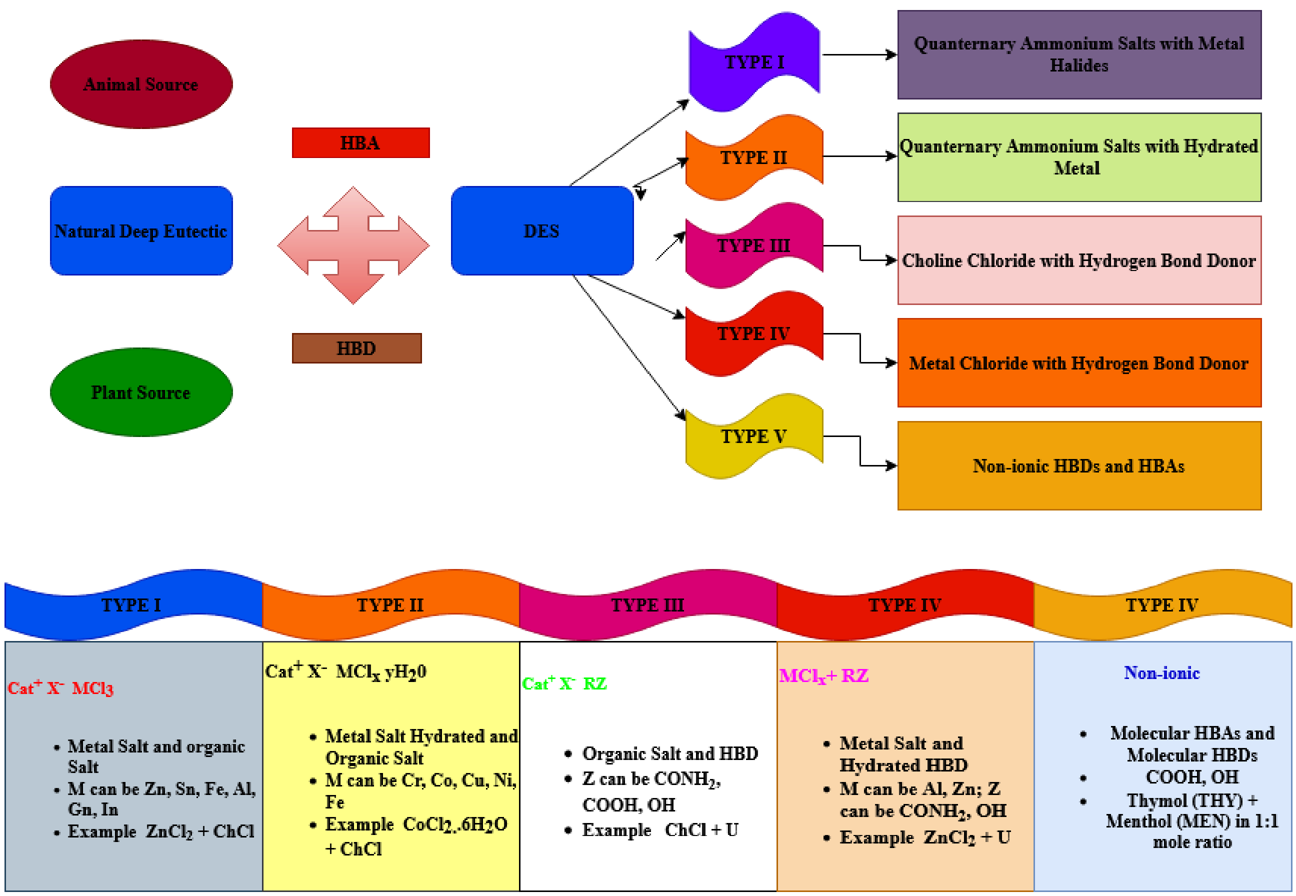

Figure 3: Deep Eutectic Solvents and Their Types

NADES has two primary sources, which fall into various categories of DES, as illustrated in Figure 3 above. Types I and II are classified as hydrophilic DES, while Types III and IV are categorized as hydrophobic DES, as explained by Zainal-Abidin et al. (2019). In Type 1 DES, metallic salts are mixed with organic salts, whereas in Type II, DES consists of metal hydrates and organic salts as hydrogen bond donors (HBDs). Type III, DES comprises a mixture of organic salts (Pelosi et al., 2023; A. Sharma et al., 2023), while Type IV, DES comprises metal chlorides and HBDs. A new categorization called Type V, DES is currently being developed and explored, which includes non-ionic molecular HBDs and HBAs. This type of DES exhibit's dominant hydrogen bonding characteristics (Abranches & Coutinho, 2022). DESs of Types I, II, and III are created by combining an ionic salt to serve as a hydrogen bond acceptor with a molecular substance acting as a hydrogen bond donor. Also, the noncovalent interactions, through the combination of molecular compounds at liquid form will form eutectic molecular liquids such as hydrogen bonding and σ-hole bonding interactions which will be DES Type IV and Type V (Yu & Mu, 2019).

Several methods can be employed to prepare DESs: heating, grinding, freeze-drying, microwave irradiation, twin screw extrusion, ultrasound-assisted, and vacuum evaporation (Ijardar et al., 2022). The commonly employed technique is heating, which involves continuous heating while stirring at about 80°C till a transparent and uniform solution is attained. Two components are combined and grounded till a precise, homogeneous liquid form is achieved (Hansen et al., 2021). Formulating a viscous and transparent substance, the freeze-drying technique combines the aqueous solutions of the HBA and HBD in the correct proportion before freezing the aqueous solutions at a lower temperature (Prabhune & Dey, 2023, M. Zhang et al., 2022). The microwave irradiation method is done by mixing the HBA and HBD mixtures in 20mL and then microwaving the combinations for 20 seconds. The twin-screw extruder is used to carry out the twin-screw extrusion procedure. TSE has rotating screws to mix DES mixtures of HBAs and HBDs, and preheating occurs at all stages (Trigui et al., 2022). Ultrasound-assisted preparation is done by adding the mixtures of HBAs and HBDs to an ultrasonic bath for 1–5 hours at 60 °C and leaving it for 24 hours (Chen et al., 2022).

The vacuum evaporation method is used for NADES. Here, the dissolved components are evaporated in a vacuum at low temperatures to produce a liquid, which is dried inside a desiccator using silica gel to attain a consistent weight (Ahmad et al., 2022). Most DESs are prepared at elevated temperatures within 50–100°C (Tu et al., 2022).

DES exhibits distinct characteristics compared to conventional organic solvents, including cost-effectiveness and lower toxicity (Janjhi et al., 2023). They are biodegradable, possess high extraction efficiency (Elahi et al., 2022), and offer a wide range of applications. DESs also demonstrate both hydrophilic and hydrophobic properties; the presence of these properties gave rise to Hydrophilic DES (HDES) and Hydrophobic DES (HDES), which make some DES nonflammable (Cao & Su, 2021; Zhang et al., 2012) and easily formed (Li et al., 2021; Ul Haq et al., 2023). These properties make them extensively used in different fields, such as biomass catalysis, purification, nanomaterial synthesis, organic material analysis, and electrochemical reactions (Rao et al., 2021). DES can be tailored as hydrophobic to be immiscible with water for water purification from pollutant analyst (Marchel et al., 2023), this hydrophobic DES could also be useful, in the development of aqueous base edible biocomposite to increase the dissolution of analytes such as cellulose in HDES. DESs offer unique physicochemical interactions with analytes, providing high selectivity in extraction and other separation processes (Momotko et al., 2022). Using DESs for their separation capabilities gives them a wide range of applications (Janjhi et al., 2023; Khajavian et al., 2022). DESs is more viscose and denser than water (Hou et al., 2023) also raising its mechanical and thermal properties (Ramli et al., 2023), HBD with relatively poor thermal stability in DES solution will decompose first, therefore DES with great stability can be achieved by selecting appropriate HBDs to form strong hydrogen bonding networking with suitable HBAs (Chen et al., 2018).

The polarity of DESs is also a key property that contributes to their versatility and unique behavior, In the study conducted Cichocki et al. (2022) DESs consisting of benzoic acid derivatives and quaternary ammonium chlorides–tetrabutylammonium chloride (TBAC) and benzyldimethylhexadecylammonium chloride (16-BAC), It was discovered that a high accuracy and precision was developed. The ability to fine-tune their polarity makes them valuable alternatives to conventional solvents for a wide range of applications across different fields, DES exhibits varying degrees of polarity based on the specific hydrogen bond donor and acceptor components used. The strength of hydrogen bonding between these components influences the overall polarity of the solvent. The advantages, disadvantages, possibilities, and risks linked to DESs are outlined in Figure 4.

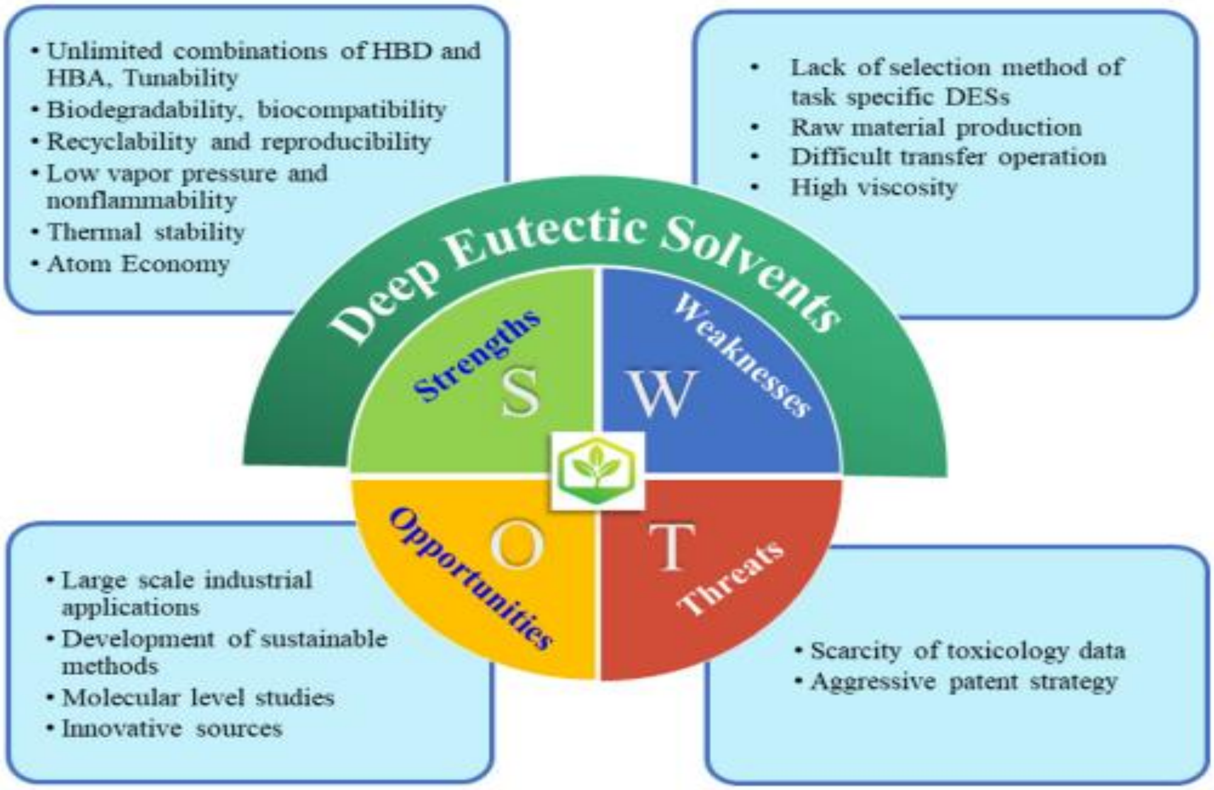

Figure 4: Strength, Weakness, Opportunity and Threats Analysis of DESs (Prabhune & Dey, 2023).

DES is in its early stages of commercial utilization, with significant industrial implementation yet to be realized. Several pilot plants have been established to explore diverse applications of DES. One notable characteristic that DES holds over other environmental friendly solvent alternatives is its ease of large-scale production, making it suitable for industrial scaling (Smith et al., 2014). The field of biocatalysis has also witnessed advancements, showing promising potential for future scaling opportunities (Guajardo et al., 2016). DESs possess a range of desirable properties, including environmental friendliness, biodegradability, non-volatility, tuneability, solubility, and nonflammability, which position them as suitable solvents for the future. It is crucial to emphasize that DESs must meet environmental and economic requirements, reusability, and regeneration; these properties are fundamental in driving the principles of green chemistry forward.

3. Dissolution of Edible Biocomposites in DESs

The mechanism of dissolving microcrystalline cellulose (MCC) in DES was investigated and attributed to the fact that HBD and HBA interact. MCC, characterized by its small particle size, has been observed to dissolve in a DES composed of 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU) as the HBA and methyl thiourea (MTU) as the HBD, in a ratio of 4:1. The dissolution process was monitored using a polarizing microscope, confirming the complete dissolution of Cellulose in DBU (Fu et al., 2020). Further studies by Sirviö et al. (2019) showed the successful production of nanocellulose or nanoparticles by dissolving Cellulose in DES containing guanidine hydrochloride and anhydrous phosphoric acid.

L-lysine hydrochloride was added to the choline liquid at a molar stoichiometric ratio of 2:1 while being stirred magnetically at 100°C to successfully dissolve the wheat straw powder in the choline chloride-based DES. The dissolution ability was enhanced by extending the processing time, employing ultrasound treatment, and heating at 90°C for 24 hours (Wang et al., 2020). Using ascorbic acid and choline chloride as DES, Liu et al. (2018) examined the extraction of tert-butylhydroquinone from food oils. Choline chloride was safe for consumption and environmentally friendly (Suthar et al., 2023). Additionally, the separation and solubility of biopolymers such as lignin, cellulose, and starch have been investigated using the solvent characteristics of DES (Abbott et al., 2005). Also Lignocellulosic substrates underwent treatment with DES, resulting in the proficient cleavage of interconnecting chemical linkages among sub-units or oligomeric constituents within the lignocellulosic polymer matrix. This process significantly advanced the overarching deconstruction of the lignocellulosic framework, thereby enhancing the facilitation of subsequent reactant infiltration poised for utilization (Tong et al., 2023). Synthesize chitin nanofibers, Li et al. (2021) studied the dissolution of chitin from crab shells using a DES based on choline chloride-thiourea. Yuan et al. (2020) successfully developed chitin nanocrystals, while Nam et al. (2023) worked on chitin nanofilms, both utilizing DES. Ascertain the dissolution of cellulose Zhang et al. (2023) employed the Kamlet-Taft Linear Solvation Energy Relationship (LSER) approach along with multivariate linear regression analysis to quantitatively assess cellulose dissolution. Coefficients were derived based on statistical significance ($p < 0.05$). The resultant correlations substantiated the efficacy of Deep Eutectic Solvents (DES) as favorable agents for cellulose dissolution.

In work by Zhu et al. (2017), different choline chloride-based DES solvents served as the HBA, while thiourea, urea, malonic acid, and glycerol served as the hydrogen bond donors and were used to recover chitin from lobster shells. Relative to the previous study on chitin extraction using DES based on choline chloride and malonic acid from lobster shells, one of the remarkable features of DES is its practical flexibility, allowing researchers to tailor solvent systems by changing one or two components of the eutectic mixture (El Achkar et al., 2021). This implies that the consumption rate of chemical components used to dissolve cellulose in the studies above must follow the World Health Organization's standards of operation to avoid it affecting the human system negatively.

4. Cellulose Structures Dissolution in DES

The structure of Cellulose in DES is influenced by the specific characteristics of cellulose and the type of DES used. Li et al. (2021) examined the crystallinity, morphology, crystal structure, and chemical structure of regenerated lignin in bagasse fibers. The pretreatment of bagasse fibers with DES resulted in noticeable changes in morphology, a slight increase in crystallinity, and an observed increase in the surface hydroxyl group of cellulose.

In another investigation by Chen et al. (2023), oxalic acid served as the HBD, while betaine, choline chloride, and N-methylmorpholine-N-oxide (NMMO) served as the HBA in DESs used to treat cellulose nanofibrils (CNF). The properties and microstructure of CNFs were examined while treated with the three different solvent types using FTIR and XRD. According to the findings, the crystal structure of CNFs remained unaltered, while the size of the crystal and crystallite increased due to the presence of hydrogen bond networks. The FTIR peaks were modified, and the analysis of two-dimensional correlation spectroscopy revealed different degrees of change in the three hydrogen bonds. The relative contents of these bonds exhibited a specific order of evolution, indicating a discernible pattern in the development of hydrogen bond networks within nanocellulose. Hydrogen bonding plays a crucial function such as affecting the solubility of the solute in solvents with higher bonding properties leads to the higher solubility of ascorbic acid in organic solvents (Hassan et al., 2019) HBA will provide good bonding sites for HBD-based electronegativity and the number of sites in DES solvent as well. The solubility of mefenamic acid solute. Organic solvents for example were influenced by hydrogen bonding and Gibbs-free energies (Abdul Mudalip et al., 2019). The solubility of cellulose in the form of MCC is considered low in TMAC and ChCl-based DES at 90°C which is < 0.66 wt%. Hydrogen bond acceptor must be improved to increase the solubility (Zhang et al., 2023).

Structural characterization plays a crucial role in understanding the creation of hydrogen bonds between the components of HBA and HBD and in evaluating the purity of the DES. FTIR is mainly used to investigate the interaction between constituents and ascertain the presence of functional groups within cells. IR analysis revealed a study of the DES formation mechanisms throughout the process (Ren et al., 2020). Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy is another widely used method for characterizing DESs and determining the molar ratio of HBA to HBD. In addition to ^{1}H NMR, conventional 13C and 13C-DEPT (distortionless enhancement by polarization transfer) methods have been utilized for DES characterization. Moreover, DESs have been analyzed using advanced two-dimensional NMR methods such as ^{1}H-^{1}H correlation spectroscopy, ^{1}H-^{1}H nuclear overhauser effect spectroscopy, COSY, and NOESY (Farooq et al., 2020). The melting point or glass transition temperature of DESs can range from 140 °C to 370 °C, depending on the DES grade, curing method, and moisture content. This temperature is frequently detected through different scanning calorimetry (DSC) tests, and thermogravimetric analysis (TGA) is used to assess the temperature stability of the DES. Polarized optical microscopy (POM) has been utilized to identify DES's HBD and HBA components since crystals are visible when DES is in a homogeneous liquid state. Elemental analysis, employed by Chao et al. (2019), measures DES's carbon, hydrogen, and nitrogen content to evaluate its purity, and theoretical principles are applied for analysis.

5. Application of DES for Future Use

Due to their environmentally friendly nature, DESs have gained popularity as alternatives to conventional solvents. Their distinctive features, including ease of preparation, versatility, and cost-effectiveness, have contributed to their widespread usage. There is a significant focus on exploring the potential applications of these non-toxic green solvents, resulting in numerous noteworthy studies and findings and exploring DESs as eco-friendly solvents. DES's characteristics include environmental friendliness, biodegradability, practical commercial preparation, cost-effectiveness, low volatility, a non-toxic substance that is not flammable, and chemically stable as displayed in Fig. 5. These have aided DES in gaining a variety of uses as a green solvent.

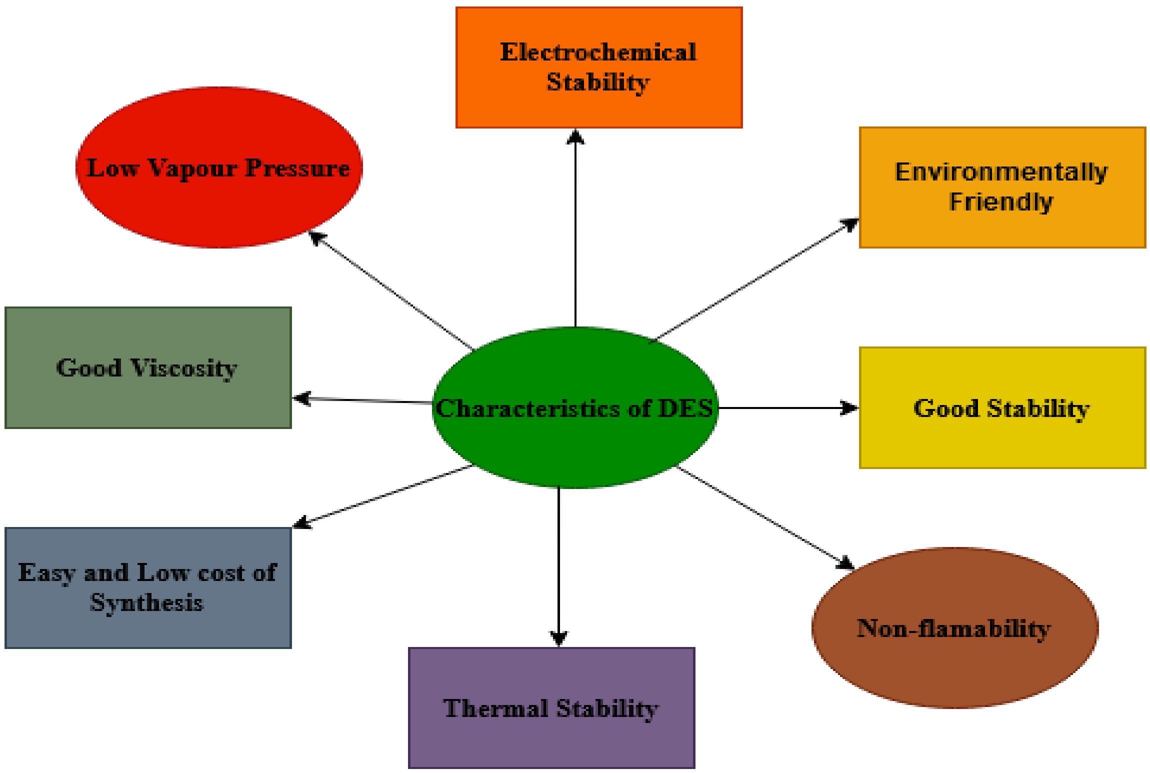

Figure 5: Characteristics of DES

5.1 Application of deep eutectics solvent in general application

A study revealed that tetrabutylammonium chloride (TBAC) as HBA and heptadecanoic acid as HBD enhanced the 1-hexanol and 1-heptanol analytes exhibited longer retention time in DES stationary phase for gas chromatography due to the interaction's formation between analytes-solvent (Momotko et al., 2021). Using organic aromatic thymol when mixed with camphor, 10-undecylenic acid and decanoic acid separately to extract polycyclic aromatic hydrocarbon (PAH), thymol camphor has extracted highest of PAH in DES mixture (Makos et al., 2018). They have found diverse applications, including biomolecule separation, removal of heavy metals, and extraction of pesticides from agricultural runoff (Van Osch et al., 2020). The incorporation of L-proline-sulfonate DES into the chitosan membrane demonstrates a promising avenue for tailoring and modifying the selectivity of methanol-methyl tert-butyl ether (MTBE) separation such good compatibility between the polymer phase and the DES thereby forming homogeneous membrane hence leading to a successful separation process (Castro-Muñoz et al., 2022). By selecting specific components for the DES formulation, it becomes feasible to fine-tune its physicochemical properties, such as polarity, viscosity, and hydrogen-bonding capacity. This tunability empowers the DES to interact differentially with various analytes or components within a mixture, affecting their partitioning behavior during the separation process. González et al. (2020) showed the enhancement of the sugar fermentation process through the extraction of phenolic chemical compounds from diluted aqueous solutions derived from biomass using menthol-based HDES. In a groundbreaking study, Sharma et al. (2021) utilized DES as functional monomers in molecularly imprinted technology, specifically employing Magnetic Deep Eutectic Solvents (MDES) to selectively recognize and separate bovine hemoglobin into a molecularly imprinted polymer (MIP).

Since DESs are part of developing ionic liquid solvents, their applications and those of ionic liquids have expanded to include electrodeposition, metal coatings, and related fields. In a notable example, a DES called "Ethaline," made of choline chloride and ethylene glycol in a 1:2 ratio, was employed for the electrodeposition of nickel (Ni) in contrast to aqueous solutions (Abbott et al., 2015). DESs have also been used in electropolishing metal surfaces, offering advantages such as high viscosity and slow diffusion, making them suitable for diffusion-controlled electropolishing processes (Kityk et al., 2020).

In a study by Millia et al. (2018), two distinct DESs, specifically L-(+)-lactic acid/choline chloride (2:1 mol/mol) and ethylene glycol/choline chloride (3:1 mol/mol), were investigated for their potential in dissolving lithium salts. These DESs demonstrated favorable characteristics, including thermal stability, high ionic conductivity, and electrochemical stability.

DESs have broad applications in synthesizing organic compounds, nanomaterials, and polymers (Tang & Row, 2013) and are used as solvents in various organic reactions (Shaibuna et al., 2022). The heterogeneous nature of DESs makes them suitable for solvothermal material synthesis, particularly in eutectic systems used as precursors (Yu et al., 2022).

DESs have shown their attributes as cost-effective alternatives for multi-chemical formulations in the pharmaceutical and drug industries. Their utilization as eutectics with active pharmaceutical ingredients has improved drug solubility, intestinal absorption, permeability, bioactivity, and controlled release (Zainal-Abidin et al., 2019). In the study conducted by Rahman et al., two novel and unconventional types of DESs, namely therapeutic DES (THEDESs) and amino-based DES (ADES), were identified. THEDESs utilize choline chloride and menthol as their key constituents and are primarily designed to enhance the efficacy of drugs. On the other hand, ADESs predominantly employ proline as their component of choice and have been explored not only for pharmaceutical applications but also for extracting phytochemicals, capturing radioactive iodine, separating oil from ores, and synthesizing bioactive compounds (Rahman et al. 2021).

In a successful large-scale application, zinc and lead were extracted from dust waste produced in the steelmaking process in an electric arc furnace using choline chloride-based DES (Abbott et al., 2009). Ali et al. (2014) conducted a pilot plant experiment to extract thiophene, effectively scaling the process from 10 g to over 1000 g; DESs were utilized in the liquid-liquid extraction method to separate aromatic compounds, exhibiting superior distribution ratio and selectivity compared to the widely used industrial solvent, sulfolane. Rente et al. (2022) utilized DES for grape anthocyanin extraction, transitioning from laboratory-scale to industrial-scale operations, potentially finding applications in the cosmetic industry. However, during the scaling-up process, the viscosity of DES poses a significant challenge, often surpassing that of conventional solvents.

Abro et al. (2022) investigated the reusability and regeneration of DESs employed in fuel oil desulfurization. Their findings revealed that the desulfurization capacity of DES decreases as the number of extraction cycles increases unless the DESs are regenerated. However, with regenerated DESs, the efficiency remains high with minimal losses. Achieving DES recyclability during extraction becomes a critical issue when scaling up operations. Temperature also plays a crucial role, impacting extraction efficiency and energy consumption. Some DESs, such as metal DES (Li et al., 2016) and ammonium DES, decrease extraction efficiency as the temperature rises, whereas oxalate DES and others demonstrate improved efficiency under elevated temperatures. Also, DESs have shown promising applications in the food industry due to their unique properties, which can offer advantages over traditional solvents and processes (Castro-Muñoz et al., 2023). More efforts are needed to recover the DES which has a high boiling point to be recovered using distillation or evaporation methods, for example, the natural deep eutectic solvent of choline-urea was recycled using hybrid membrane-based techniques (Liang et al., 2023).

5.2 Application of deep eutectics solvent in biocomposite and edible biocomposite

Edible films contain various components, such as polysaccharides, proteins, essential oils, biocomposites, and edible blends, contributing to their biodegradability, non-toxicity, and biocompatibility. Polyvinyl alcohol (PVOH), a biopolymer, has emerged as a superior choice in the production of edible films, such as coatings, due to its advantageous characteristics, including edibility, chemical stability, biocompatibility, ease of fabrication, and hydrophilicity (Thakur et al., 2022). PVOH-based edible films are available in various forms, including individual films, composites, blends, and plasticizer combinations. Notably, the successful dissolution of cashew gum into PVOH films has been achieved through DES (Bruna et al., 2021; Cha-umpong et al., 2021)

In biorefineries, DES has been employed for the pretreatment of lignocellulosic biomass, aiming to fabricate compressed-molded biocomposite panels using DES-treated fibers derived from waste materials, such as peanut shell powder, corn stover, and sugarcane bagasse. This approach has improved the strength and modulus of the compressed-molded biocomposite panels, highlighting the potential of converting agro-industrial waste into cellulose-rich wood fibers for applications in furniture and construction (Fatima Haq et al., 2022). Y. Zhang et al. (2021) stated that the adsorption process of biochar derived from p-TsOH-ChCl exhibited superior performance, both the DES and the biochar demonstrated recyclability and environmental friendliness (Ke et al. 2022). Using acidic DES in this biochar preparation presents a novel and environmentally sustainable approach for producing an efficient adsorbent. When DES is added to wet-based green tea extracts, silver nanoparticle dispersion is improved (Liu et al., 2022).

DESs were also employed as solvents in producing nanocomposite composites reinforced with chitosan-based cellulose nanowhiskers (CNW). Intermolecular solid and intramolecular hydrogen bond interaction between the chitosan matrix and the CNW filler contribute to developing a resilient structure, ultimately enhancing the performance of the biocomposite film (Chang et al., 2023). Additionally, DESs have been demonstrated to dissolve cellulose fibers from edible plants during the preparation of empty fruit bunches from oil palms through pretreatment with choline chloride-based DES (Thi & Lee, 2019).

The environmental concerns associated with non-biodegradable fossil-based food packaging, including increased solid waste generation, carbon footprint, and global warming, necessitate alternative solutions (Liu et al., 2021). In this regard, the dissolution of Cellulose in DESs for film or edible coatings has generated significant interest as an environmentally friendly packaging option. Moreover, natural deep eutectic solvents have shown potential in biochemical processes for valorizing food or agricultural waste and serving as solvents when performing catalysis, extraction, synthesis, and pretreatment (Kalhor & Ghandi, 2019). Several factors can be utilized to anticipate the suitability of compounds such as HBA and HBD components for specific applications. These factors encompass the molecular structure such as the presence of hydrogen-bonding sites, polarity, melting point, and viscosity. The hydrogen bonding action resulted from the major depression of the melting point of the DES chemical components (Hansen et al., 2021)

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6. Industrial Perspective of DES In Cellulose Processing

Scientists have shown significant interest in DESs due to their appealing physicochemical and electrochemical properties. DESs have been extensively studied as potential solvents in industrial and energy applications. With their ability to be customized by combining various HBA and HBD, earning them the term "designer solvents." Utilizing a wide range of HBA and HBD combinations, each with a different molar ratio, it is possible to modify the physical and chemical properties of DES. Factors such as temperature, water content, homogeneity of HBA and HBD, molar balance, and synthesis technique also influence DES physicochemical and electrochemical characteristics. Therefore, when utilizing DESs as solvents in different applications, it is crucial to investigate and establish an optimal equilibrium between these factors. The solvents' phase behavior, surface tension, density, ionic conductivity, specific heat, viscosity, electrochemical stability window, and environmental sustainability (green credentials) are fundamental physicochemical properties that must be explored. DES exhibits unique properties compared to other solvents commonly used for dissolving cellulose in edible or non-edible composites, biocomposites, and fibers. Due to the wide range of applications for DES, it is essential to focus on understanding how to dissolve cellulose in DES to achieve optimal results. Edible biocomposites can be derived from various edible plants.

Packaging these biocomposites is crucial for protecting against mechanical damage while incorporating additional functionalities, such as antimicrobial properties and moisture absorption. Selecting a suitable DES for the dissolution of cellulose from edible biocomposites requires considering the solubilization capacity, which is influenced by both the components of the DES and the nature of the edible biocomposites.

There is a growing interest in using DES to dissolve cellulose from edible composites and biocomposites, as well as in its application in nanomaterial and composite material preparation. However, research on the dissolution of cellulose from edible biocomposites is relatively limited. As part of the green chemistry approach, there is an expectation that suitable solvents, such as DES, will replace harmful or toxic solvents commonly used in industrial dissolution processes. Utilizing these environmentally friendly solvents, particularly in cellulose applications from edible biocomposites, holds great promise for sustainable techniques and materials.

7. Conclusion

DES shows a remarkable advancement in the realm of solvent chemistry, offering a compelling alternative to traditional organic solvents and even ionic liquids (ILs). Their extensive list of benefits, including a broad liquid range, thermal stability, low volatility, nonflammability, and the capacity for tailoring their properties to specific process requirements, underscores their versatility. Compared to ILs, DESs exhibit lower toxicity and cytotoxicity, making them a safer choice for numerous applications. Furthermore, the simplicity of DES synthesis, achieved through the precise mixing of HBA and HBD components in specific molar ratios, is a proof to their efficiency and eco-friendliness. This process generates no waste and eliminates the need for cumbersome work-up steps, translating into cost-effectiveness and reduced environmental impact for both industrial and laboratory settings. Notably, NADESs, derived from primary plant metabolites, emerge as a sustainable and greener solvent option. Their potential to replace water and lipids in essential plant processes under extreme conditions such as drought and cold further underscores their ecological significance. When it comes to dissolving cellulose in non-toxic DES solvents for edible biocomposites, the advantages become abundantly clear. DESs offer biocompatibility, biodegradability, and the ability to create eco-friendly and healthy products. To achieve successful cellulose dissolution in edible composites, biocomposites, or fibers using DES, factors like the nature of the cellulose, the type of intermolecular or intramolecular H-bond network, HBA and HBD properties, and the non-toxicity of the DES solvents must be carefully considered. In a world increasingly concerned with environmental sustainability, DESs emerge as the ideal solution for dissolving edible biocomposites, offering a bridge between advanced technology and responsible ecological practices. This review has illuminated the potential of DES in cellulose dissolution, highlighted the key determinants of their toxicity, and emphasized their wide-ranging applications in our ever-evolving world. As we move forward, DESs hold the promise of revolutionizing various industries while promoting a greener, healthier, and more sustainable future.

Author Contributions

Chigozie Charity Okwuwa: Conceptualization; writing – original draft; review and editing. Fatmawati Adam: Conceptualization; supervision; writing – review and editing. Farhan Mohd Said: Writing – review and editing. Michael E. Ries: Validation; writing – review and editing.

Declaration of Competing Interest

The authors state that they have no known competing financial or personal interests that could have influenced the work reported in this study.

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