

# Chapter 10

## Use of Deep Eutectic Solvents in Nanotechnology

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Deep eutectic solvents (DES) are specialized solvent systems obtained by mixing two or more components in specific mole ratios, with a melting point significantly lower than the melting points of their pure components. This class of solvents, which entered the literature in 2003 when Abbott et al. described the choline chloride-urea system, has become an integral part of nanotechnology research over the past two decades. DESs; While it offers a well-established alternative to traditional organic solvents with features such as adjustable polarity, low volatility, high solvency capacity, biodegradability, and low cost, it also has serious technical, and regulatory limitations such as high viscosity, moisture sensitivity, and limited ecotoxicological data. Furthermore, the potential of DESs in nanotechnological applications stems from several key advantages: reduction of volatile organic solvents, solubility, control of morphology, surface functionalization capacity, and broad electrochemical efficacy.

The areas where DESs are used in nanotechnology are metal and metal oxide nanoparticle synthesis, carbon-based nanomaterial processing, drug nanocarrier systems, metal-organic frameworks (MOF), nanocomposites, and electrochemical applications. In conclusion, while DESs hold the potential for real transformation in nanotechnology, extensive research investments are needed to realize this potential on an industrial, and biomedical scale.

## 1. Introduction

The design, production, characterization, and functionalization of matter in dimensions of approximately 1-100 nm, and its use in many disciplines (such as materials science, chemistry, medicine, and energy technologies) cause nanotechnology to come to the fore. However, materials used at the nanoscale need to be evaluated not only in terms of technological efficiency but also in terms of resource efficiency, environmental impact, and human health.

In the synthesis of nanomaterials, high-energy conditions such as surfactants, organic solvents, strong reducing agents, and high temperatures used in traditional methods are fundamental processes. Organic solvents used in these processes have limitations such as flammability, toxicity, difficulty in recovery, and negative environmental impacts. The occurrence of negative effects on biological, and ecosystems brings the “green nanotechnology” approach, which is a sustainable, and safe alternative in nanomaterial production, to the fore. The green nanotechnology approach includes utilizing renewable resources, reducing or eliminating toxic solvents, and adopting principles that will not harm the life cycle by providing more moderate living conditions (Huston et al., 2021)

These principles can directly influence the properties of nanomaterials, such as solvent selection, particle size, crystal structure, morphology, dispersion stability, and biocompatibility. All these features bring deep eutectic solvent (DES) to the fore, blended with a more controlled, and sustainable production model.

## 2. Discovery, and Significance of Deep Eutectic Solvents

Throughout the 20th century, organic solvents such as chloroform, dichloromethane, toluene, acetone, and DMF were mainly used in all synthesis, and production stages. However, these solvents have caused air pollution due to their high volatility, ecosystem disruptions due to their bioaccumulation potential, and serious occupational health risks due to their carcinogenic properties. The US Environmental Protection Agency (EPA) defines most of these solvents in the ‘volatile organic compound’ (VOC) category; The European REACH regulation considers them on the list of substances of high concern (SVHC) (Anastas & Warner, 2000).

With the acceleration of the green chemistry movement in the 1990s, supercritical CO<sub>2</sub>, water, and ionic liquids (ILs) entered the research agenda as alternative solvents. The limited biodegradability of ionic liquids, which is the most popular solvent class of these solvents, high production costs, and ecosystem toxicity in some systems have led to a shift towards different solvent systems (Smith & Abbott, 2014).

Abbott et al. (2003) found that the melting point was only 12°C with a mixture of choline chloride (ChCl, melting point 302°C), and urea (melting point 133°C) in a mole ratio of 1:2 (Figure 1). The chloride anion (Cl<sup>-</sup>) forms simultaneous hydrogen bonds with both NH<sub>2</sub> groups of the urea molecule, while the choline cation (Ch<sup>+</sup>) provides additional interactions through the hydroxyl group. This network structure disrupts the crystal lattice of both choline chloride, and urea. This situation was explained by the intense hydrogen bonding interaction between the two components, and this system was called the “deep eutectic solvent (DES)”.

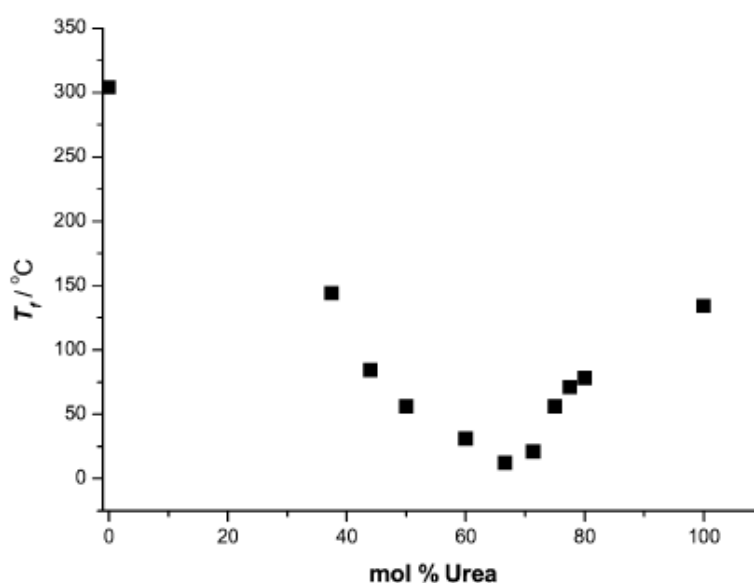


Figure 1. Freezing point of choline chloride/urea mixtures as a function of composition

(Abbott et al., 2003).

By mixing two or more components in certain proportions, DES systems have a melting point that is lower than the melting points of their components. This significantly lowers the Gibbs free energy, improving the stability of the mixture in the liquid phase.

The occurrence of this behavior in DES systems can often be explained by strong hydrogen bonds, Lewis acid-base interactions, ion-dipole interactions, and charge delocalization (Hansen et al., 2021). Hydrogen bond acceptor (such as HBA; choline chloride, tetraalkylammonium salts), and hydrogen bond donor (HBD; ethylene glycol, glycerol, urea, lactic acid, carboxylic acids, sugars, amino acids, and phenolic compounds) are used in DES systems (Figure 1). In these systems, the diversity of components enables properties such as viscosity, pH, polarity, conductivity, hydrophobicity, biocompatibility, and coordination capacity to be designed as desired (Smith et al., 2014).

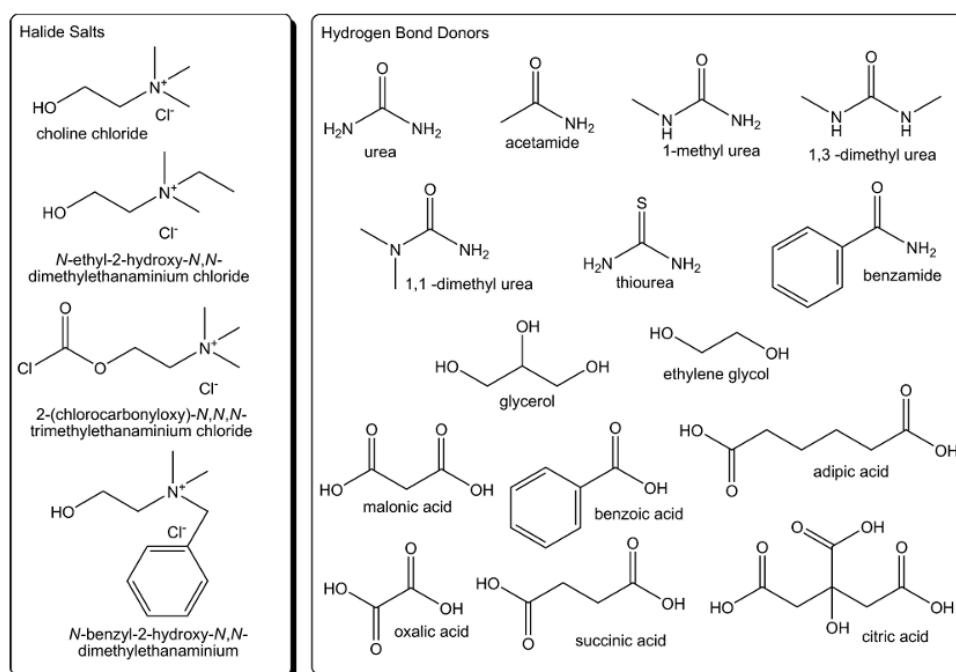


Figure 2. Structures of some halide salts, and hydrogen bond donors used in the formation of deep eutectic solvents (Smith, Abbott & Ryder, 2014)

In this context, the ease of preparation of DESs compared to ionic liquids, the fact that the majority of raw material bases are food-based, and their low costs are the basis for their preference in industry and laboratory-based studies (Paiva et al., 2014).

## 2.1. Classification, and Component Types of DES

DESs are categorized into 5 types according to their various eutectic combinations (Figure 2). Its general formula is  $\text{Cat}^+\text{X}^-\text{zY}$ .

$\text{Cat}^+$ ; ammonium, phosphonium or sulfonium cation,

X<sup>-</sup>; The halide ion (usually Cl<sup>-</sup>)

Y; Lewis or Brønsted acid

z; the number of Y molecules involved in the complexation of anionic species.

Although the initial classification put forward by Abbott et al. (2004) included four types, the rapid development of the field has significantly expanded this scheme. Currently, NADES, hydrophobic OBDs, and multicomponent systems are considered separate categories (Dai et al., 2013; van Osch et al., 2015).

### 3. Physicochemical Properties in the use of DESs in nanotechnology

#### 3.1.1. Viscosity, and Mass Transfer

Many DES systems exhibit markedly high dynamic viscosity compared to conventional organic solvents, and water at room temperature (Hansen et al., 2021). This high viscosity; nucleation, and growth kinetics, solute diffusion, mixing efficiency, pressure loss in processes requiring pumping, and scale-up design adversely.

Several strategies are reported for the solution of the viscosity problem (Smith et al., 2014).

a) With the controlled addition of water, the hydrogen bond network in the DES system can be partially disrupted, and the viscosity can be reduced.

b) Although raising the temperature produces an Arrhenius-type viscosity reduction, this can increase the energy cost, and the risk of degradation of some DES systems.

c) Microwave, and ultrasound-assisted processing methods are able to improve reaction kinetics, and mass transfer over conventional mixing methods.

d) The design of low-viscosity DES systems aims to minimize viscosity disadvantage.

#### 3.1.2. Polarity, Solvency, and Tunability

One of the remarkable features of DES systems is that they can be designed in a wide polarity range, and their solvency ratio can be adjusted by changing their components. Thanks to this tunability, the solubility of organic molecules, polymers, biomolecules, inorganic metal salts, and hydrophobic drug compounds can be increased (Zhang et al., 2012; Perna et al., 2020).

From a nanotechnological point of view, two key areas of application play a decisive role:

Solubilization of highly concentrated nanoparticle precursors of metal salts increases the efficiency of the reaction.

Solubilization of functional groups to be used in surface modification in DES media helps to control surface chemistry.

### 3.1.3. Ionic Conductivity, and Its Electrochemical Activity

The ionic structures of DES systems are fundamental in applications such as electrodeposition, battery electrolytes, electrochemical sensors, and supercapacitors (Abbott et al., 2004; Hansen et al., 2021). The broad electrochemical activity of these systems, particularly the deposition of metals such as Zn, Cr, and Al in aqueous environments, is why some metals are preferred in the electrodeposition process. However, the ionic conductivity of DES systems is mostly inversely proportional to their viscosity; designing DES to ensure this balance is a precursor for electrochemical applications.

### 3.1.4. Thermal Stability, and Moisture Sensitivity

The majority of DES systems have thermal stability in the range of 100–200°C, providing an adequate operating range in nanomaterial synthesis processes (Smith et al., 2014). However, in Type III DES systems, moisture can alter the viscosity, ionic conductivity, and solvency profile of the medium. This is because ambient moisture disrupts the hydrogen-bond network by absorption into the DES structure. This creates the problem of repeatability in process design.

## 4. Structural Characterization Methods of DESs in Nanotechnology Applications

In order for DESs to be used reliably in nanotechnology applications, their structural (crystalline, morphological, etc.), and dynamic properties must be fully understood. Various analytical techniques are employed for this purpose (Ponce et al., 2023).

**NMR Spectroscopy:** Since the formation of DES systems relies heavily on interactions between hydrogen acceptor, and hydrogen donor structures,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR assays enable the monitoring of interactions, and chemical shift changes between structure components. In particular, expansions or density changes in the signals of -NH, -OH, -COOH or amide protons provide information about chemical shifts, and hydrogen bonds. The spectra obtained by dissolving in  $\text{D}_2\text{O}$  or  $\text{DMSO-d}_6$  reflect the strength of hydrogen bonding (Delso et al., 2019).

**Fourier transform infrared spectroscopy (FTIR):** It is one of the widely used methods for DES formation, and determination of the activity of surface functional groups in DES-functionalized nanomaterials, and for determining the interactions between functional groups with hydrogen bonds. Changes in shift, wavenumber, band expansion, and intensity of the C=O, O-H, and N-H stress bands are effective in determining hydrogen bond formation (Alotaibi et al., 2024).

**UV-visible spectroscopy:** It can be used to monitor the formation of nanomaterials during synthesis, to monitor synthesis kinetics, to pre-evaluate colloidal stability, to determine the localized surface plasmon resonance of metal nanoparticles, and to calculate the optical bandgap of semiconductor nanomaterials. For example, in plasmonic metal nanoparticles such as Au, and Ag, wavelength shift in absorption peaks in relation to particle size, shape, aggregation state, and surface environment acts as a change in peak intensity or peak expansion (Lee et al., 2008; Amendola et al., 2017).

**Transmission Electron Microscopy (TEM):** It is used to examine the properties of nanomaterials such as primary particle shape, size, and size distribution, internal structure properties, crystal planes, and lattice fringes in detail. It also enables evaluation of nanomaterials using selected-area electron diffraction (SAED) for characterization of polycrystalline, single-crystal, or amorphous structures. For this reason, it is recognized as one of the most powerful imaging techniques for the synthesis of DES-supported metal, metal oxide, carbon, and magnetic nanoparticles, as well as for verifying results (Mourdikoudis et al., 2018; Joudeh & Linke, 2022).

**Scanning Electron Microscopy (SEM):** It is used to obtain information about the topography, surface morphology, agglomeration state, distribution of particles on the surface, crack or porosity structure, coating homogeneity, and film morphology of nanomaterials. The use of SEM in conjunction with the EDS/EDX detector provides information to determine the surface morphology of nanomaterials, as well as their elemental composition, and the distribution of elements on the surface (Rades et al., 2014; Mourdikoudis et al., 2018).

**Small Angle X-ray Scattering (SAXS):** Monitors nanoparticle growth kinetics within DES in real-time. That is, it helps to provide statistical information about the size, shape, size distribution, aggregation state, and growth mechanism of nanostructures (Raghuwanshi et al., 2014).

**Dynamic Light Scattering (DLS):** A standard method for nanoparticle size distribution, and zeta potential measurement. It is especially used to evaluate surface charge, dispersion stability, and the behavior of DES-functionalized nanoparticles in the application environment (Bhattacharjee, 2016).

## 5. Using DES in the Synthesis of Nanoparticles

### 5.1. General mechanism of nanoparticle formation

The general mechanism of nanoparticle formation in the DES environment can be evaluated within the framework of the following stages (Wagle et al., 2014; Abo-Hamad et al., 2015):

**Precursor dissolution, and complexation:** Metal salts dissolved in DES form coordination complexes with HBA, and HBD molecules. This complexation affects the reactivity and reduction potential of the metal ion.

**Nucleation:** The high viscosity of DES contributes to homogeneous nucleation under diffusion control.

**Growth:** Growth occurs by diffusion of ions in the environment into the crystal nucleus. The viscosity of the DES restricts the diffusion rate, slowing the growth kinetics.

**Stabilization:** DES components that adsorb to nanoparticle surfaces, providing electrostatic, and steric stabilization. This adsorption layer prevents particles from coalescing, complicates surface characterization, and can influence biological interactions.

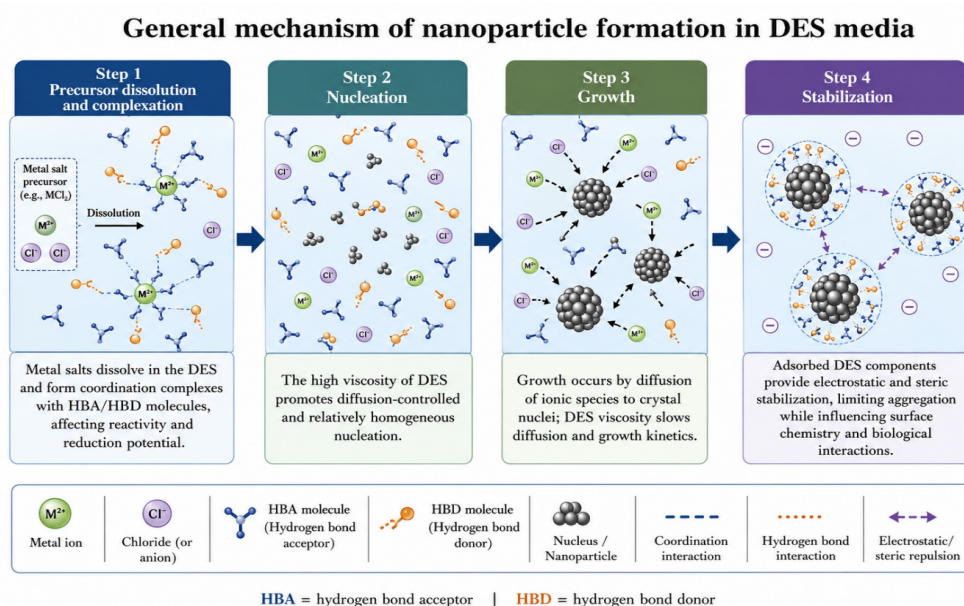


Figure 3. General mechanism of nanoparticle formation in DES media

## 6. DES systems, and Nanomaterials

DES systems are used in the fields of solvent media, electrodeposition, electroless deposition, nanocatalytic, nanofluidic, reticular nanomaterials, and functionalization in the preparation of nanomaterials (Figure 4). The studies, which have accelerated since the mid-2010s,

cover a wide range of materials from gold, and silver to platinum group metals, and from metal oxides to bioceramics.

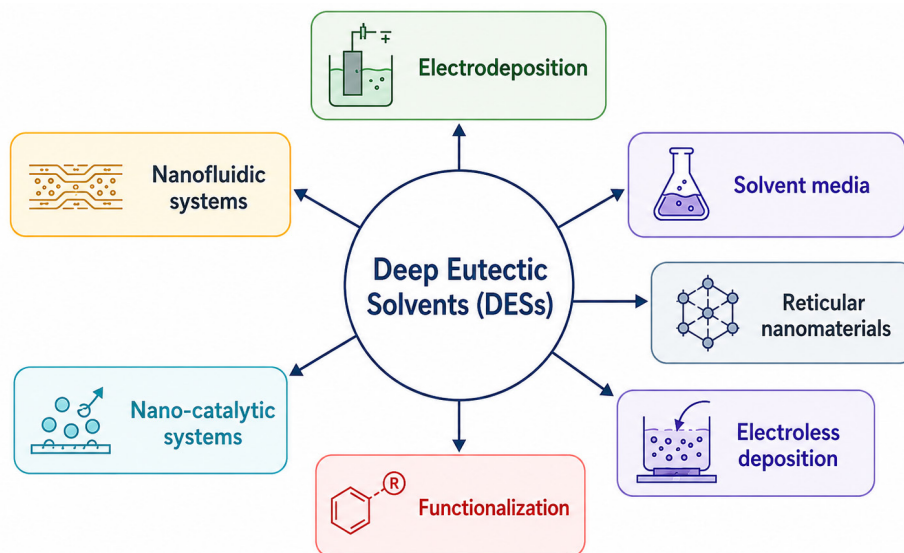


Figure 3. The application fields of DESs for nanomaterials (Nam et al., 2023)

## 6.1. Synthesis of Metal Nanoparticles

Synthesizing metal nanoparticles in the DES system has been developed as an alternative to classical organic or aqueous solvent-based methods. In addition to being solvents, DES systems are responsible for dissolving metal ions, regulating reduction behavior, controlling nucleation rate, and stabilizing the nanoparticles formed on the surface.

Studies have shown that especially the choline chloride (ChCl) anion can form complexes with metal ions; hydrogen bonding donors that can affect the solvation environment, and kinetics of metal precursors include ethylene glycol, urea, glycerol, and ascorbic acid. These DES systems play an active role in the shape, size, crystal surface, and agglomeration tendency of metal nanoparticles. It has been stated that DES systems are used as solvents in the reaction medium for the synthesis of gold, silver, magnetic nanoparticles, ZnSe, CZTS (Copper–zinc–tin chalcogenide,  $\text{Cu}_2\text{ZnSnS}_4$ ), and different biopolymer nanoparticles, and provide significant advantages (Nam et al., 2023). In the formation of metal nanoparticles, metal ions are generally reduced, and turned into neutral metal atoms, and then these atoms participate in the nucleation-growth process.

High viscosity in DES environments slows the diffusion of metal species. This can provide controlled morphological follow-up in nucleus growth. The high ionic strength, and low surface tension of DES systems can affect nucleation rate, and surface stabilization. In addition, it is possible to use it in the production of metals, alloys, and composite nanomaterials due to its high electrochemical stability, good solubilization of precursors, and templating/capping effects in DES systems (Brandão & State, 2026)

Studies on metal nanostructures synthesized in the DES environment of silver nanoparticles (AgNPs) are of great importance. DES environments offer suitable environments for solubilizing metal ions, regulating nucleation, and controlling particle growth in the synthesis of AgNPs. Smaller, and more uniform particle formation has been reported in some such AgNPs syntheses (Wagle et al., 2014). It has been noted that DES systems, such as ChCl-ethylene glycol, and ChCl-glycerol, can be used as electrolytes or reaction media in AgNPs synthesis (Brandão & State, 2026).

Gold nanoparticles (AuNPs) are among the fundamental materials in biomedical imaging, thermal treatment, and molecular recognition owing to their plasmonic properties, chemical inertness, and surface functionalization capacity. In the study cited on the synthesis of AuNPs in DES media, it was stated that AuNPs were obtained in different morphologies by reducing  $\text{HAuCl}_4$  in ethaline or reline medium using reducing agents such as  $\text{NaBH}_4$  or ascorbic acid (Wagle et al, 2014). In ChCl-ethylene glycol DES medium, synthesis of AuNPs was reported in another study, obtained by reduction of  $\text{HAuCl}_4$ . In this process, it has been stated that the DES environment plays an active role in the solubility, reduction behavior, nucleation, and growth processes of metal precursors (Azzouz & Hayyan, 2023).

In the synthesis of copper-based nanoparticles, the DES medium offers a practical alternative. In ChCl-urea DES medium, the synthesis of CuCl nanoparticles was carried out, and the effects of parameters such as the presence of polyvinylpyrrolidone (PVP), ascorbic acid/CuCl molar ratio, and mixing method on nanoparticle formation were evaluated. It has been shown that metal salt reduction and particle stabilization can be accomplished at low temperatures in the DES environment (Huang et al., 2013).

DES systems appear to be effective for metal nanoparticle synthesis, including dissolving metal precursors, adjusting the reduction potential, orienting crystal surfaces, controlling particle nucleation, and reducing agglomeration. Therefore, in the production of metal nanoparticles such as Cu, Ag, Au, Pd, and Pt, the desired product can be obtained by optimizing factors such as DES composition, HBA/HBD ratio, water content, temperature, and reducing agent type.

## 6.2. Synthesis of metal oxide, and magnetic nanoparticles

Metal oxide nanoparticles are used in sensors, photocatalysis, energy storage, environmental treatment, and biomedical applications. Metal oxide nanoparticle synthesis can generally be performed in DES by sol-gel, solvothermal, ionothermal, antisolvent-assisted precipitation, and electrochemical methods. The DES system is active in the dissolution of the metal precursor, the formation of hydroxide/oxide intermediates, and the regulation of crystal growth. The formation of metal oxide can be explained in general by the conversion of metal ions into hydroxide interphase, and then into metal oxide structure by dehydration/crystallization processes. During the control of these steps, the water content, viscosity, hydrogen-bond structure, acidic/basic character, and coordination interactions with metal ions in the DES medium are effectively controlled.

Brandão, and State (2026) noted that among the methods used in the synthesis of metal oxide nanoparticles are electrochemical methods with solvothermal or sol-gel. In another study carried out in DES systems (ChCl:urea), it was shown that syntheses were performed by dissolving commercial ZnO powders, and then precipitating them in water/ethanol antisolvent media at different rates, producing materials with different ZnO nanoparticle morphologies. It has been stated that the antisolvent composition, and the injection rate of the DES phase constitute the fundamental parameters in the nucleation, and growth steps (Zhang et al., 2012). It has been reported that rice-like structures, granular particles, twin cones, nanorods, and nanorod-flower-like ZnO structures form when these parameters are changed (Wagle et al., 2014).

In a study conducted by Chen et al., spiral  $\text{Fe}_3\text{O}_4$  nanoparticles used in magnetic separation, Fenton-like catalysis, drug delivery, and targeted biomedical systems were prepared by coprecipitation of  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$  ions in ChCl-urea DES medium; spherical  $\text{Fe}_3\text{O}_4$ -DES magnetic nanoparticles of approximately 10.5 nm in size were synthesized (Chen et al., 2013). In another study in which magnetic iron oxide synthesis was performed, the DES-electrolysis method was used. In the method, water-soluble magnetic iron oxide nanoparticles were synthesized using choline chloride, choline phosphate, and urea as a DES. Here, iron atoms are converted to  $\text{Fe}^{+3}$  ions on the anode surface, and oxygen, and iron oxide nanocrystals are formed from the decay of DES components. At the same time, the amine groups formed in the environment from the DES components are also attached to the nanoparticle surface. This results in the formation of surfaces that are hydrophilic, with long-term colloidal stability, and high zeta potential (Brandão & State, 2025).

### 6.2.1. Use of DES in the Synthesis of Carbon-Based Nanomaterials

Carbon-based nanomaterials are used in energy storage, sensor, catalysis, environmental adsorption, and biomedical-based applications due to their properties such as high surface area, electrical conductivity, chemical stability, mechanical strength, and surface functionability. However, graphene-based structures, and carbon nanotubes tend to agglomerate due to strong van der Waals interactions. This makes dispersion control, and surface modification of structures critical. DES systems enhance the effectiveness of structures by interacting with carbon surfaces through ionic interaction, hydrogen bonding,  $\pi$ - $\pi$  interaction, and surface wetting effects.

Functionalization of carbon nanotubes with DES enables the formation of oxygenated functional groups such as -OH, -COOH, and C=O on the carbon nanotube surface, thereby increasing surface area, dispersion stability, and interaction with pollutants; thus supporting their use in environmental nanotechnology. In environmental nanotechnology, DESs are used in the synthesis or modification of carbon nanotubes, graphene oxide, magnetic iron oxides, and similar nanomaterials in the adsorption, and degradation of water pollutants such as dyestuffs, pharmaceuticals, metal ions, and pesticides (Ponce et al., 2023).

DES-functionalized carbon nanotubes (CN) / multi-wall nanotubes (MWCNT) play an active role in adsorption capacity, and surface functionalization. Nam et al. stated in the review

that phosphonium-based DES systems of CNT surfaces can be used for arsenic, and mercury removal (Nam et al., 2023).

In reduced graphene oxide, and graphene oxide (GO) systems, DESs can be used as coupling agents, in nanocomposite synthesis, or as functionalization media aids. It is stated that ChCl: urea solvent is used as a coupling agent in the preparation of  $\text{Fe}_3\text{O}_4$ -graphene oxide nanohybrids, and the resulting nanohybrids are used for Pb(II), and methylene blue removal (Ponce et al., 2023). In addition, in the same review,  $\text{Ni}_3\text{V}_2\text{O}_8$ /N-doped reduced graphene oxide hybrids were formed with the ChCl:oxalic acid DES system, and GO/ZnO photocatalytic structures were formed with the ChCl:ethylene glycol DES system. It is reported that the presence of DES in the formed structures improves morphological, and structural properties, and contributes to adsorption or photocatalytic performance (Ponce et al., 2023).

### 6.2.2. Use of DES in electrochemical nanoparticle synthesis

DES systems can be used in electrochemical nanoparticle synthesis as an alternative to traditional aqueous electrolytes, and some ionic liquids. In the production of electrochemical nanomaterials, properties such as low vapor pressure, low surface tension, high precursor solubility, and high ionic strength make DES systems advantageous. For example, he states that low surface tension provides a high nucleation rate, and high ionic strength plays an active role in particle size distribution, and morphology through templating, capping, and stabilization effects (Brandão & State, 2026).

Nanomaterials consisting of Au, Ag, Pt, Pd, Ni, Te, and different alloys can be prepared in DES media through electrodeposition. Parameters such as applied potential, electrolyte temperature, electrochemical species concentration, current density, and electrolyte surface affect the morphology of the obtained nanomaterials. By adjusting such parameters, nanostructures with complex morphologies, such as nanowires, nanoflowers, concave tetrahedra, and similar structures, can be obtained. Bimetallic systems such as Cu-Ag, Pd-Ag, and Au-Pt can be tuned by electrochemical parameters to form porous or nanocrystalline structures (Brandão & State, 2026).

In the DES system, low mass transfer due to high viscosity in electrochemical nanoparticle synthesis, low ionic conductivity in some systems, solvent recovery, and scale-up difficulties are encountered.

Table 1.

## Examples and Usage of DES in nanotechnology

| DES system           | Molar ratio       | Main role in nanotechnology              | Representative nanotechnological application                                                                                | Ref.                                      |
|----------------------|-------------------|------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| ChCl:Urea            | 1:2               | Electrolyte/reaction medium              | Electrodeposition of Ni, Pd, and Te nanostructures; preparation of metal, and metal hydroxide nanomaterials                 | Nam et al., 2023; Brandão & State, 2026   |
| ChCl:Urea            | 1:2               | Green medium for nanoparticle synthesis  | TiO <sub>2</sub> nanoparticles, and photocatalytic nanomaterials                                                            | Azzouz & Hayyan, 2023                     |
| ChCl:Urea            | 1:2               | Functionalization agent                  | DES-functionalized MWCNTs for electrochemical sensing, including nitrite detection                                          | Azzouz & Hayyan, 2023                     |
| ChCl:Urea            | 1:2               | Electrolyte / stabilizing medium         | Pd nanoparticles, and Pd-based 2D superstructures; Hydrogen Evolution-related Electrocatalysis                              | Nam et al., 2023                          |
| ChCl:Urea            | 1:2               | Dispersant / nanofluid base fluid        | SiO <sub>2</sub> -based DES nanofluids for desulfurization                                                                  | Nam et al., 2023                          |
| ChCl:Ethylene glycol | 1:2               | Electrolyte / electrodeposition medium   | Ni films, Ni-SiO <sub>2</sub> nanocomposite coatings, Te nanostructures, and metal matrix nanocomposites                    | Nam et al., 2023; Tomé et al., 2018       |
| ChCl:Ethylene glycol | 1:2 or 1:3        | Electropolymerization / sensing medium   | Poly(methylene blue) or poly(brilliant cresyl blue)-based CNT-modified electrodes for sensing applications                  | Azzouz & Hayyan, 2023                     |
| ChCl:Glycerol        | 1:2<br>1:3<br>1:4 | Dispersant / nanofluid base fluid        | TiO <sub>2</sub> -, Fe <sub>2</sub> O <sub>3</sub> -, CuO-, SiC-, and carbon-based DES nanofluids for heat-transfer systems | Nam et al., 2023                          |
| ChCl:Glycerol        | 1:2               | Solvent / reducing or stabilizing medium | Ag nanoparticles, and other metal nanoparticle systems; Carbon Nanotube Dispersion                                          | Ponce et al., 2023; Azzouz & Hayyan, 2023 |

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| DES system                                   | Molar ratio | Main role in nanotechnology                   | Representative nanotechnological application                                                            | Ref.                  |
|----------------------------------------------|-------------|-----------------------------------------------|---------------------------------------------------------------------------------------------------------|-----------------------|
| ChCl:Glycerol                                | 1:2         | Dispersant                                    | Single-walled carbon nanotubes for CO <sub>2</sub> adsorption, and carbon-based nanomaterial processing | Azzouz & Hayyan, 2023 |
| ChCl:ZnCl <sub>2</sub>                       | 1:2         | Nanoconfinement / Lewis-acidic medium         | DES-based poly(furfuryl alcohol)-grafted CNTs; Electrocatalytic Glucose Detection                       | Azzouz & Hayyan, 2023 |
| ChCl:p-Toluenesulfonic acid                  | 1:2         | Structure-directing agent / reaction medium   | Chemically synthesized nanoparticles, and morphology-controlled nanomaterials                           | Tomé et al., 2018     |
| ChCl:Malonic acid                            | 1:1         | Structure-directing medium                    | Chemical synthesis of nanoparticles, and carbon-based structures                                        | Tomé et al., 2018     |
| ChCl:Ascorbic acid                           | 2:1         | Extractant / reducing-support medium          | Magnetic iron nanoparticles from iron salts; Biohydrogen-related nanomaterial applications              | Azzouz & Hayyan, 2023 |
| ChCl:Phenol                                  | 1:2         | Impregnation agent                            | DES-impregnated Ag nanoparticles for Pb(II) extraction from edible oils                                 | Azzouz & Hayyan, 2023 |
| Tetra-n-butylammonium bromide:Glycerol       | 1:4         | Functionalization / oxidation-assisted medium | DES-functionalized MWCNTs for Ni <sup>2+</sup> removal from water                                       | Ponce et al., 2023    |
| Methyl-triphenylphosphonium bromide:Glycerol | 1:3         | Functionalization agent                       | DES-functionalized CNTs for As <sup>3+</sup> removal                                                    | Ponce et al., 2023    |
| Benzyltriphenylphosphonium chloride:Glycerol | 1:16        | Functionalization agent                       | DES-functionalized CNTs for arsenic adsorption                                                          | Ponce et al., 2023    |
| Cetyltrimethylammonium bromide:Glycerol      | 1:2         | DES functionalization medium                  | CNT/ZnCo <sub>2</sub> O <sub>4</sub> -based adsorbent for eosin dye removal                             | Ponce et al., 2023    |

| DES system                                | Molar ratio | Main role in nanotechnology                   | Representative nanotechnological application                                                         | Ref.                  |
|-------------------------------------------|-------------|-----------------------------------------------|------------------------------------------------------------------------------------------------------|-----------------------|
| Glycine:Fructose                          | 1:3         | NADES-based functionalization agent           | NADES-functionalized celite/ polyethylene glycol hydrogel nanocomposite for phosphate adsorption     | Azzouz & Hayyan, 2023 |
| Tetrabutylphosphonium bromide:Formic acid | 1:1         | Surface functionalization agent               | DES-coated CeO <sub>2</sub> nanoparticles for CO <sub>2</sub> capture                                | Azzouz & Hayyan, 2023 |
| Tetraethylammonium chloride:Thymol        | 1:1–1:5     | Carrier / stabilizer                          | Magnetic nanoparticle-based ferrofluids for dispersive micro-solid-phase extraction                  | Azzouz & Hayyan, 2023 |
| Thymol:Menthol                            | 1:1         | Hydrophobic Type V DES / extraction medium    | Hydrophobic nanoplateforms, water-immiscible extraction systems, and potential nanoformulation media | van Osch et al., 2019 |
| Decanoic acid:Quaternary ammonium salt    | Variable    | Hydrophobic DES / water-immiscible extractant | Extraction-oriented hydrophobic systems; potential coupling with nanomaterial-assisted separation    | van Osch et al., 2015 |

## 7. Conclusion

DES has the potential for real transformation in nanotechnology, owing to its tunable physicochemical properties, wide range of components, relatively easy preparation procedures, and multifunctional chemical capabilities. When the existing literature discussed in this section is examined, it is seen that DESs make unique, and valuable contributions in the basic application areas of nanotechnology such as green nanoparticle synthesis, lipid, and polymeric nanocarrier systems, carbon-based nanomaterials, metal-organic frameworks, nanocomposites, and electrochemical energy systems.

The strongest, and most well-documented contributions of DESs to nanotechnology can be summarized under the following headings: reduction or substitution of volatile organic solvents, electrodeposition of reactive metals through broad electrochemical activity, particle morphology, and size control through the tunability of solution chemistry, co-solvent, and

solubility enhancer functions in lipid, and polymeric nanocarrier systems. These additives position DESs as a legitimate solvent alternative for consideration in nanotechnology process chemistry.

Biobased raw material origin, energy, and waste balance of the synthesis process, ecosystem toxicity, recovery efficiency, and regulatory compliance are critical parameters that determine the true sustainability of DES-based technologies, and should be evaluated through comprehensive life cycle analyses. The most critical research agendas ahead of the field are; development of standardized preparation, and characterization protocols, creation of comprehensive toxicological, and ecotoxicological databases, scaling engineering studies, and preclinical safety studies.

As a result, DESs are considered a platform that can make a real contribution to the sustainable transformation of nanotechnology. However, for this contribution to be fully realized, it requires multidisciplinary research collaborations, rigorous methodological standards, honest assessments of limitations, and an evidence-based regulatory framework. The integration of these frameworks with scientific rigor, environmental responsibility, and clinical safety principles is the decisive condition for the long-term success of DES-based sustainable nanotechnology.

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