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Review

Deep eutectic solvents for the production and application of new materials

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ABSTRACT

The search for both new and sophisticated materials that meet the needs of the modern era, and for sustainable eco-efficient processes, has raised deep eutectic solvents (DES) to a prominent place. Research focused on the use of these solvents – highly advantageous in economic, practical, and environmental terms – for the creation of innovative materials has been growing fast, and a very large number of publications reporting the use of DES as valuable alternatives to overcome the limitations of conventional solvents, and even ionic liquids, has been published. DES have proved to offer tremendous opportunities and have opened new perspectives to produce novel and refined materials.

This review focuses on recent advances concerning these new materials and on the practices that have been developed employing DES as solvents. The definition, preparation and unique properties of DES are first addressed, followed by a more extensive description of their applications in polymer, metal deposition and nanomaterial science and sensing technologies. Their impact in the production processes and in the properties of the materials obtained, as well as their key role as designer solvents, is highlighted.

1. Introduction

The increasing demands for eco-friendly processes within the framework of green and sustainable chemistry, and the recognition of remarkable and advantageous properties of deep eutectic solvents (DES) have led, in the past two decades, to a growing interest in the use of these mixtures as alternatives to conventional organic solvents and to their predecessors ionic liquids (IL) in numerous and diverse fields. It is not, thus, surprising that since the pioneering work of Abbott [1–3], a number of reviews describing the synthesis, properties and applications of DES has been published [4–14]. Nevertheless, these reviews do not concentrate on the materials' aspects and, given the large number of articles that is being published, need updating.

This review is divided into three main sections: definition, preparation and properties, and applications of DES. Only a summary of the relevant information concerning definition, preparation and properties will be given, covering in more detail the most recent advances. Since the terms DES and IL have sometimes been used interchangeably, and there has been much debate in the literature on the frontiers between the definitions of these two types of solvent, some considerations on the subject DES vs IL will be made. Because the number of promising applications of DES for materials synthesis has been growing constantly, a complete and up-to-date description of the potential applications of DES will be provided.

2. Definition and types of DES

DES are commonly defined as systems composed by a mixture of at least two components, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), which are able to self-associate to form a new eutectic phase characterized by a melting point (below 100 °C) lower than that of each individual component. These constituting components should additionally possess safe characteristics, low toxicity, renewability and biodegradability as well as low cost. A schematic representation of the formation of a deep eutectic solvent is given in Fig. 1.

DES have often been described by the formula Cat^+-X^-zY, in which Cat^+ is the cation of any ammonium, sulfonium, or phosphonium salt, and X^- is a Lewis base, generally the halide anion of the salt [6]. Y is either a Lewis or Bronsted base, and z is the number of

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Abbreviations: API, active pharmaceutical ingredient; AFM, atomic force microscopy; BET, Brunauer–Emmett–Teller; ChCl, choline chloride; CNT, carbon nanotubes; DES, deep eutectic solvent; DLS, dynamic light scattering; EDS, energy dispersive spectroscopy; EG, ethylene glycol; FESEM, field emission scanning electron microscopy; FTIR, Fourier transform infrared; HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; IL, ionic liquid; MIP, molecular imprinted polymer; MIT, molecular imprinted technology; NADES, natural deep eutectic solvents; NMR, nuclear magnetic resonance; PEDOT, poly(3,4-ethylenedioxythiophene); PL, photoluminescence; PMB, poly(methylene blue); PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; QCM, quartz crystal microbalance; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TGA, thermogravimetric analysis; THEDES, therapeutic deep eutectic solvents; VSM, value stream mapping; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

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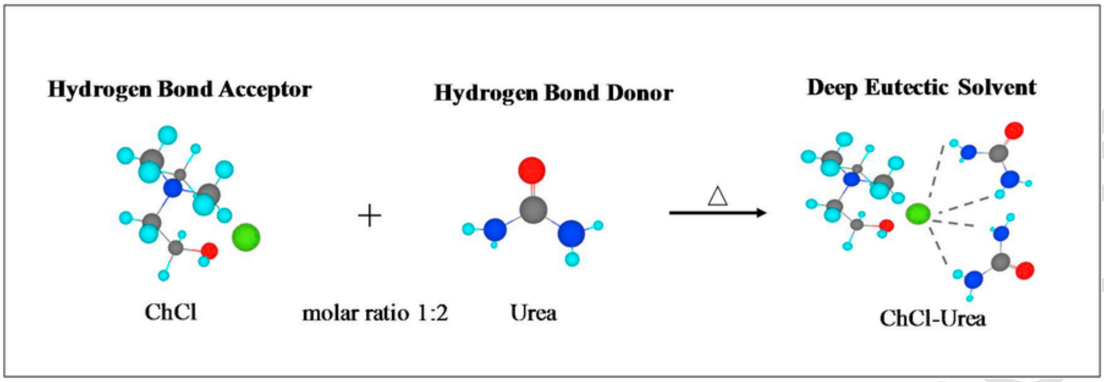

Fig. 1. Schematic representation of the formation of a deep eutectic solvent, illustrated with ChCl and urea.

Y molecules. Complex anionic species are formed between X^- and Y. The main interactions between the halide salt or HBA and HBD are essentially hydrogen bonds, though occasional electrostatic forces and van der Waals interactions are also likely to be established [4]. Experimental and theoretical studies [15] have shown that, in general, the highest fraction of hydrogen bonds in DES are intramolecular and occur between the HBD and the halide anion. The anion-HBD hydrogen bond network is the basis for the fundamental properties of DES (see Section 4 below). A comprehensive discussion of these features has been provided in a recent review [14].

In 2017, new insights derived from computational studies have been flourishing [16–18]. Quantum mechanical molecular dynamics simulations were performed on choline chloride (ChCl)/urea, ChCl/ethylene glycol (EG) and ChCl/glycerol systems to investigate the nanostructure of the DES and the interactions between the ions [16]. The results obtained were used to explain the differences in eutectic point temperatures and viscosity. HBD acidity, HBD structure/conformation and the extent of HBD self-interaction are all factors that together originate different hydrogen bond networks in the DES, determining their structure. ChCl/urea shows a well-established hydrogen bond network between the salt and HBD, leading to a higher melting point and a significantly higher viscosity. On the other hand, the structure of the bulk HBD is largely preserved for ChCl/glycerol and ChCl/EG, resulting in a smaller melting point depression. The oversaturation of HBD groups in the bulk, and consequently a more extensive HBD self-interaction, is responsible for the higher viscosity of ChCl/glycerol compared to the other eutectic mixtures. Zhekenov [18] also explained the role of inter- and intramolecular hydrogen bonding in these DES, using molecular dynamics simulation methods. The data suggest that that the formation of these DES relies on intermolecular hydrogen bonds between the constituent species and simultaneously a reduction in the number of hydrogen bonds established between the constituent components. This decrease in the number of hydrogen bonds and also in the interaction energies between the components leads to a lower melting point. Additionally, by evaluating the effect of water on these DES, the authors concluded that although water molecules form hydrogen bonds with ions and HBD, at low mole fractions they are absorbed into the molecular matrix of the DES and hence do not affect diffusion of ions. At higher mole fractions, water stifles intermolecular and intramolecular interactions in DES and thus, the properties change severely. Further studies on ChCl/urea eutectic mixtures by ab initio molecular dynamics simulations [17] revealed that, contrary to prior suggestions, besides hydrogen bonds between all constituents, there is also a similar spatial distribution between the chloride anion and the oxygen atom of urea close to the cation core of choline, due to a similar charge located in both atoms. The huge number of possible identical interactions leads to a larger entropy and to a low melting point of the liquid phase. The hydroxyl-chloride interactions are rigid and possess the longest lifetime of all hydrogen bonds. Fast HBA dynamics is aided by the *trans* hydrogen atoms of the carbonyl group of urea which contributes to the low meting point of the ChCl/urea mixture.

The number of possible combinations of HBA and HBD that are able to form eutectic mixtures is extremely high, and many have been reported to date. In order to rationalize the properties and behaviour of these solvents, the classification into four types of DES (Table 1) has often been considered: Type 1 (quaternary salt and metal halide), Type II (quaternary salt and hydrated metal halide), Type III (quaternary salt and hydrogen bond donor) and Type IV (metal halide and hydrogen bond donor) [6,8,13,19]. The common components of DES are depicted in Fig. 2.

Among the types listed, the majority of studies has focused on quaternary ammonium cations, which are known to be safe, cheap and non-toxic, used in combination with compounds capable of creating hydrogen bonds such as amides, acids and alcohols. Indeed, since the first descriptions of the eutectic phenomenon by Abbott et al. based on studies of mixtures of urea and choline chloride [1–3], a very large number of articles on DES formed by ChCl with urea, ethylene glycol or glycerol, usually in 1:2 molar ratios, has been published, though other types of DES have also been proposed, but to a lesser extent. Excellent reviews up to 2016 provide full descriptions of all DES types, along with complete discussions of the HBA and HBD combinations that have been employed to create DES [4,6–10,13,14]. Table 2 contains an up-to-date and chronological summary of the main DES that have been prepared. There are two particular classes of DES that have been recently gaining increasing attention: natural deep eutectic solvents (NADES) and therapeutic deep eutectic solvents (THEDES). Their interesting characteristics and attractive promising applications justify a more detailed description of these types of eutectic solvent (Sections 2.1 and 2.2).

Table 1
The main types of DES (from ref [6]).

Type	Formula	Terms
I	$Cat^+X^-\ z\mathrm{MCl}_x^-$	M: Zn, Sn, Fe, Al, Ga, In
II	$Cat^+X^-\ z\mathrm{MCl}_x{\cdot}y\mathrm{H_2O}$	M: Cr, Co, Cu, Ni, Fe
III	$Cat^+X^-\ z\mathrm{RZ}$	Z: $CONH_2$, COOH, OH
IV	$\mathrm{MCl}_x + \mathrm{RZ} = \mathrm{MCl}_{x-1}{}^+{\cdot}\mathrm{RZ} + \mathrm{MCl}_{x+1}$	M: Al, Zn; Z: $CONH_2$, OH

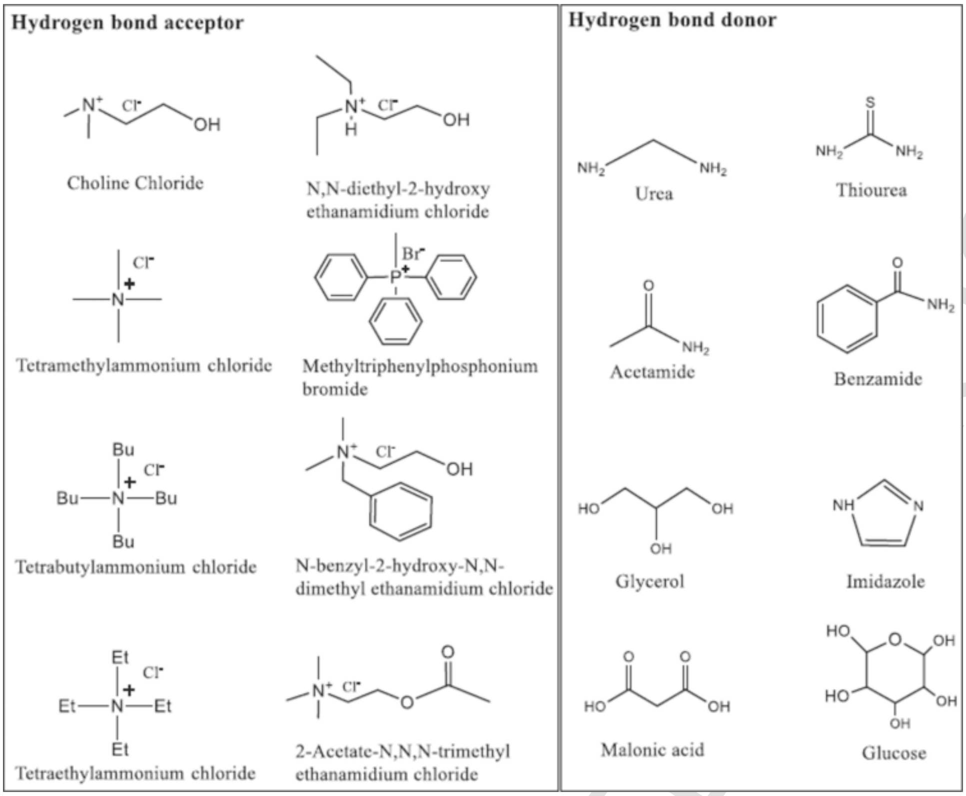

Fig. 2. Examples of common HBA and HBD usually employed.*From* [14], *reproduced by permission of Elsevier.*

2.1. NADES

In 2011, as a result of an attempt to explain the solubility of intracellular compounds that are insoluble in water and lipid phases, Choi [43] reported the discovery of a completely new class of DES, which he designated as natural deep eutectic solvents (NADES). These are mixtures containing combinations of metabolites that occur in large amounts in cells, with a crucial role in biological processes such as cryoprotection, drought resistance, germination and dehydration. Questioning whether NADES were the third liquid phase in living organisms, over 30 combinations of cellular constituents were prepared and the solubility of natural products (flavonoid rutin, paclitaxel, ginkgolide B, salmon DNA, albumin, starch) in those mixtures evaluated, finding that in most cases the solubility in NADES was remarkably superior to that in water. The hypothesis proposed by Choi was later confirmed by Dai et al. in 2013 [44], when the authors provided further evidence for NADES as an alternative medium to water for solubilizing, storing and transporting non-water soluble metabolites in living cells and organisms. Mixtures of ChCl with a variety of natural products such as ChCl/organic acids or alcohols or sugars, organic acids/sugars, amino acids/organic acids or sugars were assessed, resulting in the discovery of more than 100 NADES. NMR spectroscopic investigations revealed the existence of hydrogen bonding between the constituents. Solubilization studies of a wide range of non-water soluble biomolecules (e.g. gluten, DNA, starch) in the novel NADES showed a higher solubility than in water. The presence of NADES in plants was also explored. Further studies performed in 2013 [45] and 2014 [46] reinforced NADES as prospective extraction media for bioactive compounds, as well as stabilizing agents. Yields between 75% and 97% were obtained for the extraction of phenolic compounds from *Carthamus tinctorius* L. using organic acid/sugar or amino acid and ChCl/sugar or alcohol eutectic mixtures [45]. Natural pigments from safflower were shown to be more stable in sugar-based NADES than in water or 40% ethanol solution, due to the establishment of strong hydrogen bonds between solutes and NADES molecules [46].

In the following years, a plethora of biorenewable, biodegradable and non-noxious materials from the classes of organic acids, sugars, amino acids, choline and urea were tested as NADES components, as testified in recent papers and reviews [47–51], and nowadays the term has been unambiguously established. In 2017 Xin et al. [49] synthesized NADES from trehalose and ChCl, and showed, using FTIR spectroscopy and NMR, the strong hydrogen bonding interactions between trehalose and ChCl. They investigated the thermostability of lysozyme in the NADES and discovered that it was significantly enhanced in some trehalose/ChCl mixtures, proving that NADES are adequate candidates for stabilizing mixtures.

The future role of NADES in the food, cosmetic and pharmaceutical industries has been repeatedly pointed out, and these solvents have often been successfully applied in extraction and separation processes [45,50,51].

2.2. THEDES

Introduced in the context of pharmaceutical sciences, the term therapeutic deep eutectic solvents (THEDES) has been defined as bioactive eutectic systems composed of an active pharmaceutical ingredient (API) as one of the DES constituents [53]. The interest in these systems relies on their potential use as improved pharmaceutical formulations, to overcome issues associated with drug solubility and permeability.

Table 2
The main DES found in the literature, with year of first use.

Year	DES	Method	Ref.
2003	ChCl/urea	Direct mixing and stirring of the components at 80 °C	[2]
2004	ChCl/carboxylic acid	Direct mixing and stirring of the components at 100 °C	[3]
2007	Metal salts/alcohol or amides	Direct mixing and stirring of the components at 100 °C	[20]
2009	ChCl/urea	Freezing–drying method	[21]
2012	ChCl/fructose	Direct mixing and stirring of the components at 400 rpm and 80 °C	[22]
2013	ChCl/D-glucose	Direct mixing and stirring of the components at 400 rpm and 80 °C	[23]
2013	ChCl/phenol ChCl/o-cresol ChCl/2,3-xylenol	Direct mixing and stirring of the components at 40 rpm and 80 °C	[24]
2014	Tetrapropylammonium Br/EG Tetrapropylammonium Br/triethyleneglycol Tetrapropylammonium Br/glycerol	Direct mixing and stirring of the components at 400 rpm and 80 °C	[25]
2014	1-Butyl-3-methylimidazolium Cl/$ZnCl_2$/acetamide 1-Butyl-3-methylimidazolium Cl/$ZnCl_2$/urea	Heating mixtures at 100 °C	[26]
2014	Guanidine HCl/urea Guanidine SCN/urea	Direct mixing and stirring of the components at 70 °C and 60 °C, respectively	[27]
2015	$ZnCl_2$/urea	Direct mixing and stirring of the components at 80 °C	[28]
2015	ChCl/$ZnCl_2$ N,N-diethylethanolammonium Cl/$ZnCl_2$ ethyltriphenylphosphonium Br/$ZnCl_2$ tetrabutylphosphonium Br/$ZnCl_2$	Mixing the components mechanically in a jacketed vessel at 90 °C	[29]
2015	Tetra-n-butylphosphonium Br/$FeCl_3$	Direct mixing and stirring of the components at 270 rpm and 80 °C	[30]
2015	$MnCl_2$/acetamide $MnCl_2$/glycerol $MnCl_2$/D-glucose $MnCl_2$/D-fructose	Direct mixing of the components at 80 °C	[31]
2015	Methyltriphenylphosphonium Br/tetraethyleneglycol benzyltriphenylphosphonium Cl/tetraethyleneglycol allyltriphenylphosphonium Br/tetraethyleneglycol ChCl/tetraethyleneglycol N,N-diethylethanolammonium Cl/tetraethyleneglycol	Direct mixing and stirring of the components at 350 rpm and 80 °C	[32,33]
2015	Biodiesel waste-glycerol/ChCl	Stirring ChCl in crude glycerol at 80 °C	[34]
2016	ChCl/$CaCl_2 \cdot 6H_2O$	Direct mixing and stirring of the components at 400 rpm and 90 °C	[35]
2016	1-Methylimidazole/propanoic acid 1-Methylimidazole/nitric acid Diethanolamine/propanoic acid	Direct mixing and stirring of the components with magnetic stirrer at 50 °C	[36]
2016	ChCl/levulinic acid Ch acetylchloride/levulinic acid Tetraethylammonium Cl/levulinic acid Tetraethylammonium Br/levulinic acid Tetrabutylammonium Cl/levulinic acid Tetrabutylammonium Br/levulinic acid	Direct mixing of the components at 80 °C	[37]
2016	Betaine/urea	Direct mixing of the components	[38]
2016	ChCl/phenol/$FeCl_4$ ChCl/EG/$FeCl_4$	Direct mixing of the components at room temperature and at 802 °C, respectively	[39]
2017	ChCl/phenylacetic acid	Direct mixing and stirring of the components at 35/50 °C	[40]
2017	ChCl/urea/glycerol ChCl/urea/malic acid	Direct mixing of the components at 80 °C	[41]
2017	ChCl/p-toluenesulfonic acid ChCl/trichloroacetic acid ChCl/monochloroacetic acid ChCl/propionic acid	Direct mixing and stirring of the components at 80 °C	[42]
2011–2017	NADES with various formulae		[43–51]
2017	THEDES		[52–57]

The first report on THEDES was published by Stott et al. [54] in 1998, who prepared a mixture composed of menthol and ibuprofen, envisaging the enhancement of skin permeation and development of a transdermal delivery system. In 2009 [55], significant increases in the solubilities of benzoic acid and of the drugs danazol, griseofulvin and intraconazole in ChCl/urea and ChCl/malonic acid were reported, and in 2014 [56] an eutectic system containing lidocaine/ibuprofen was proposed for the development of transdermal delivery systems. Recently, Duarte et al. investigated a novel THEDES based on ChCl/menthol complexed with three APIs: acetylsalicylic acid, benzoic acid and phenylacetic acid [57], and further explored it in [52]. The interactions between the THEDES constituents were examined by NMR, revealing that the DES is formed by hydrogen bonds established between menthol and the API. It was concluded that the solubility and permeability of the APIs when in the THEDES can be remarkably improved, suggesting that these systems provide a more efficient delivery of the APIs.

In spite of the still small amount of structural and functional information on THEDES available up until now, their potentialities in pharmaceutical engineering will certainly lead to an exponential exploitation of these systems in the near future.

2.3. DES vs IL

IL first appeared at the beginning of the 20th century but their importance as convenient green alternatives to common organic solvents was only recognized much later [58–61]. Despite the early enthusiasm, testified by the boom in publications in the decade 2000–2010 [59,60,62], some of their initially assumed advantageous characteristics soon started to be questioned [60–62]. In this context, DES emerged as versatile substitutes for conventional IL, and were initially treated as a new generation of IL [4]. Although they have similar physicochemical properties to IL, DES differ from IL in three main aspects [4–7,9–14]. First, the potential for scale-up: IL are expensive, and some of them present high toxicity, as well as having poor biodegradability, biocompatibility and sustainability [60–62]. In contrast, DES have lower costs and a much-reduced environmental impact. Secondly, the preparation processes of IL and DES are quite different. While DES are synthesized by simply mixing the components, generating no waste and requiring no purification steps, the preparation of IL is far more difficult and expensive. Finally, IL are composed entirely of ions, that interact through ionic bonds; DES are the result of complexation between a HBA and a HBD whose interactions, as discussed above, involve mostly hydrogen bonds.

3. Preparation and properties of DES

From a practical and experimental point of view, DES are generally prepared by mixing HBA and HBD at an appropriate temperature, in one of two ways: (1) the lower melting point component is first melted, and then the higher melting point compound is added to the liquid, and the mixtures are melted together; (2) the two components are mixed and melted together, when both constituents have high melting points. Since the original work of Abbot in 2003 [2], where the solid starting materials ChCl and urea were heated at a 2:1 molar ratio to obtain a mixture that was liquid at room temperature, many DES have been prepared, as reviewed in [9] and [13]. More details are given in Table 2.

For the correct design of DES, and to rationally expand their applications, a detailed understanding of the physical properties of these solvents is of the utmost importance.

Generally speaking, DES are characterized by low melting points, low volatility, non-flammability, low vapour pressure, dipolar nature, chemical and thermal stability, high solubility, tuneability, low toxicity and biodegradability [4]. However, since these solvents are chemically tuneable, their properties can be tailored to build task-specific DES, according to the applications envisaged, with different physicochemical properties. Data for the phase behaviour, density, viscosity, conductivity, surface tension, ionicity, electrochemical behaviour, toxicity and environmental impact of numerous DES have been provided, and very complete databases are available in the literature [4,6,8,9,13,14].

Very recently, systematic experimental studies on the effect of the cation alkyl chain length on the physical properties of DES have been carried out using mixtures of alkylammonium bromide salts and glycerol [63] or urea [64]. The results obtained suggest that the length of the cation alkyl chain has little effect on composition-dependent properties (density, refractive index, thermal conduction), but profoundly affects properties where intermolecular (ionic) forces play a role, such as viscosity, surface tension and interfacial structure, and significantly influences the melting point depression. The effect of HBD on the physical properties of benzyltriethylammonium chloride based DES has also been the focus of systematic investigations [65], performed by experimental measurements of the freezing points, pH, viscosity, refractive index, conductivity and density of the eutectic mixtures. The effect of the identity of the HBD was reported to be rather considerable. Computational approaches using molecular dynamics simulation methods [66] unravelled the behaviour of DES based on the mixing of choline chloride salt with glycerol, levulinic acid, malonic acid, phenylacetic acid, and urea in static and dynamic external electric fields (EEF). A larger molecular mobility was observed in intense fields than that of fluids in the absence of EEF. Structural perturbations were found to be small for all of the DES investigated, but significant decreases in molecular diffusion under high frequency fields were detected.

Other very recent publications provided updated data for the density, viscosity and conductivity of ChCl/EG eutectic mixtures at atmospheric pressure and at temperatures between 35 °C and 90 °C [67], for rheological, thermodynamic and gas solubility properties of phenylacetic acid-based DES [40]. The density, electrical conductivity, dynamic viscosity, refractive index for the acidic DES ChCl/p-toluenesulfonic acid, trichloroacetic acid or monochloroacetic acid or propionic acid were measured in [42], and the density, viscosity, pH, refractive index, conductivity and excess thermodynamic properties of ChCl/glycerol and ChCl/EG, as well as of mixtures of these two eutectic solvents were evaluated in [68].

A brief final comment on NADES. Comparatively few physicochemical characterizations of this particular class of DES is available [47,49]. In 2016 [47], a comprehensive body of data on NADES based on ChCl, organic acids, amino acids and sugars was published. Values for the density, thermal behaviour, conductivity and polarity for more than 100 NADES were provided. In 2017, Xin et al. [49] reported physicochemical properties for ChCl/trehalose DES. Nevertheless, the relative paucity of physicochemical data for NADES has not enabled a deep understanding of NADES at a molecular level up until now.

4. Main applications of DES

Having established themselves in the last couple of decades as convenient green alternatives to aqueous and conventional solvents, the potential applications of DES have been widely explored. The major research efforts have been focused in mainly three fields: polymer, metal processing and nanomaterials sciences. In the following sections, we will present a detailed review of the materials prepared with the use of DES in these three areas.

4.1. Application of DES in polymer science

Despite the currently widely-recognized potentialities of DES in polymer science, the application of these media for the preparation of polymeric materials with enhanced functional, structural and morphological characteristics is a relatively recent research topic, and thus still rather unexplored. Although, in the last couple of years, a large amount of work has been dedicated to this subject, there are very few reports that date back before 2012. DES have been essentially used in polymer science as solvents, functional additives and monomers. Here, the characterization of polymer materials prepared in DES is provided, and their applications are presented in detail. The advantages of DES relative to other conventional solvents are also emphasized.

4.1.1. As solvents

DES have been extensively applied as solvent media in polymer synthesis.

Choline chloride (ChCl)/urea DES have been employed for the preparation of polymers with important applications in medicine [69] and industry [70]. For instance, a polyoxometalate (POM) with anti-HIV activity was successfully isolated from ChCl/urea mixtures at room temperature [69], in a relatively short time, in what was reported as a more convenient, simplified, easier, more rapid and environmentally friendly process, which avoids the disadvantages of poor solubility, low yields and noxious organic solvents in previous methods. The polymeric material obtained was characterized by XPS, IR, UV–vis spectroscopy, TG analysis, X-ray diffraction and single crystal X-ray diffraction, as well as by cyclic voltammetry, revealing high-quality POM aggregates. ChCl/urea was used as a catalytic curing agent for epoxy resins based on the low molecular weight diglycidyl ether of bisphenol A [70]. The role of the eutectic mixtures was analyzed using FTIR, rheometry and differential scanning calorimetry, and described as a biodegradable and sustainable catalytic curing agent for epoxy resins.

Among the few examples reported, the use of DES for the fabrication of coordination polymeric compounds is given in [71]. Two lanthanide coordination polymers were synthesized ionothermally from a 1:2 molar ratio of ChCl/EG or ChCl/urea mixture. The structural single crystal X-ray diffraction and photoluminescence studies performed on the prepared compounds showed a helical chain structure and the typical lanthanide luminescence. The method was recognized as an advantageous and efficient approach.

Innovative and up-to-date publications related to the area of nanotechnology can be found in [72] and [73]. A 1:2 molar ratio of (2-hydroxyethyl)trimethylammonium chloride/urea was investigated as an alternative solvent medium for the production of agar nano and micro fibres, using the electrospinning technique [72]. The influence of agar-in-DES on the fibre morphology was assessed by SEM (Fig. 3). Improved viscoelasticity and mechanical resistance were observed compared to agar-based fibres prepared in water or polyvinyl alcohol, proving that the choice of solvent is decisive for the electrospinning process. An efficient and green approach to prepare multifunctional polymer monoliths with incorporated carbon nanotubes in a mixture of an IL and ChCl/EG eutectic solvent has been described [73]. The

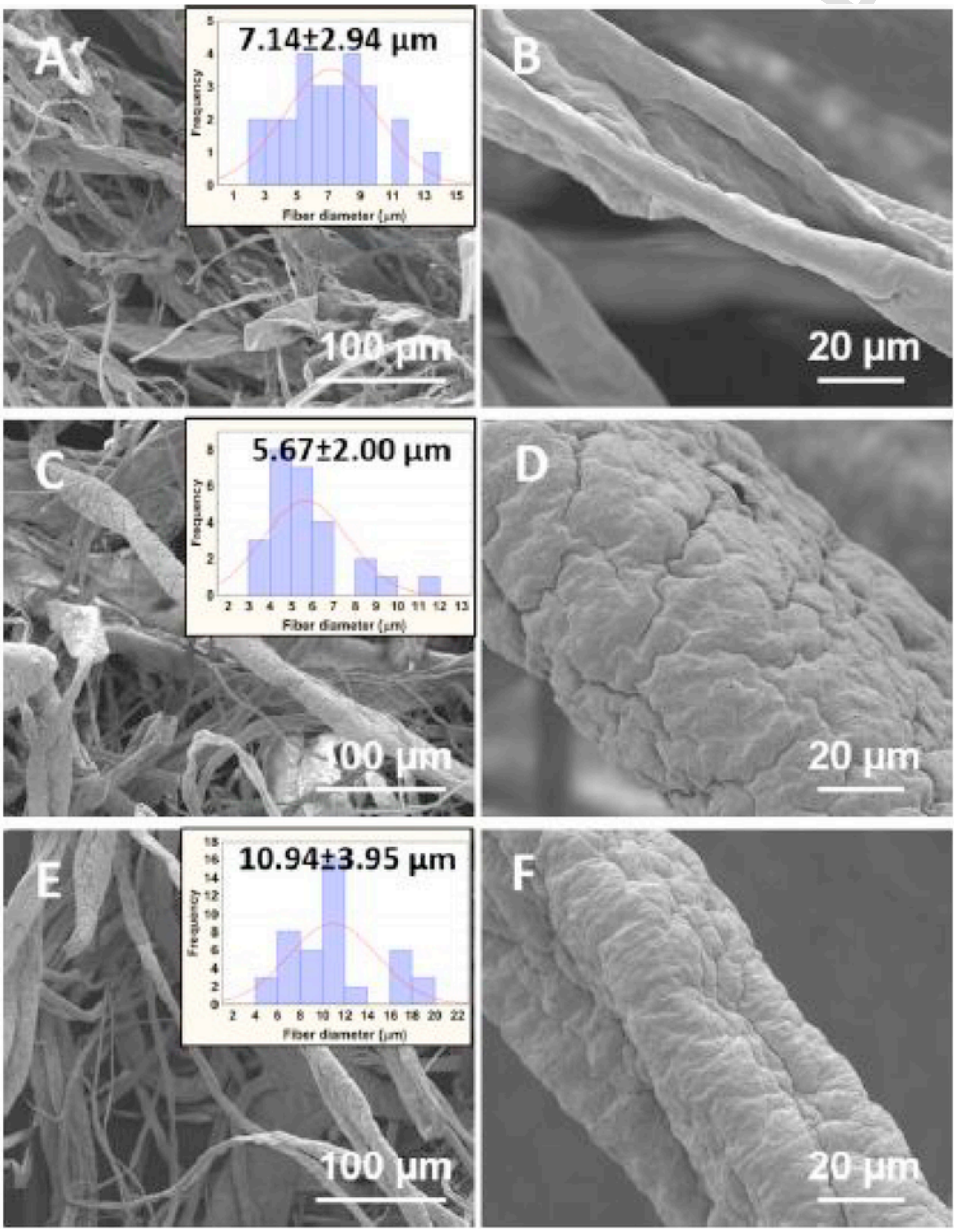

Fig. 3. Representative SEM micrographs of agar-in-DES fibres obtained using a 1:2 molar ratio (2-hydroxyethyl)trimethylammonium chloride/urea eutectic mixture, at 500× (A, C and E) and 2500× (B, D and F) magnifications. The respective fibre diameter distributions are shown as insets.*From* [72]*, reproduced by permission of Elsevier.*

polymer monoliths obtained were studied by capillary electrochromatography, and it was shown that their morphology can be tuned by the composition of the IL/DES mixture to provide separation ability for small molecules such as alkyl phenones and alkyl benzenes.

The application of DES media in the electrochemical synthesis and deposition of conducting polymers has lately become an interesting research theme [74–78]. Polyaniline was synthesized in a 1:2 ChCl/1,2-ethanediol mixture, using potentiodynamic and potentiostatic electrochemical procedures [74]. The authors underlined the sustainability, low cost, efficiency and green character of the process. The morphology and the optical properties of the polyaniline films prepared were evaluated by SEM and UV–vis spectroscopy, exhibiting nanoparticulate morphology, high reversibility and excellent conductivities. PEDOT:PSS films were synthesized in ChCl/urea eutectic media [75], which acted as surface treatment reagents to improve the thermoelectric properties of the conducting polymer produced. The results obtained indicate that DES are advantageous choices as surface treatment reagents for conducting polymer thermoelectric materials.

Brett et al. have reported the use of eutectic mixtures as convenient media for the electrodeposition of polymers for the modification of glassy carbon electrodes (GCE), to be employed as electrochemical sensors [76–78]. EDOT was electropolymerized in eutectic mixtures composed of ChCl and ethyleneglycol, glycine or urea, and the PEDOT modified GCE were characterized by cyclic voltammetry, electrochemical impedance spectroscopy and SEM (Fig. 4) [76]. PEDOT/GCE prepared from ChCl/urea and ChCl/EG showed encouraging electrocatalytic and morphological properties, and were successfully applied as sensors for ascorbate. Subsequent work on the application of PEDOT-modified GCE as biomarker sensors, constructed by the electrodeposition of the polymer in the eutectic solvents ChCl/urea, ethylene glycol or glycerol [77] further proved the advantageous sensing characteristics when compared to those of PEDOT-modified GCE prepared in aqueous solutions. Very recently, the synthesis of nanostructured PMB polymer films on GCE, carried out by electropolymerization from ChCl/EG eutectic mixtures, was investigated [78,79]. It was shown by SEM studies that the scan rate used during electropolymerization was a key factor in determining the structure and morphology, and thus the electrochemical properties, of the PMB films. In addition, the PMB films obtained in DES exhibited better sensing performance for ascorbate, when compared to those prepared in aqueous media.

4.1.2. As functional additives

Besides acting as solvents, DES can also work as templates and/or ligand suppliers. The suitability of DES as plasticizers for a wide range of polymeric (bio)compounds has been investigated [80–85]. ChCl/urea and ChCl/glycerol eutectic mixtures were incorporated as additives in the preparation of corn starch- [80] and cellulose- [81,83] based polymer electrolytes, as well as in the fabrication of agar films [82]. The use of DES for corn starch and cellulose modification showed advantages such as sustainability, low cost and lower toxicity of the plasticizing processes, as well as superior morphological, conducting, thermal and chemical integrity characteristics of the natural polymer electrolytes [80,81,83]. The agar films had good mechanical resistance and enhanced elasticity compared with typical aqueous agar films, as revealed by diffusion and SEM data [82]. Globally, the DES with the best modification ability was ChCl/urea, assuring efficient plasticization of the materials. Moreover, more compact and homogeneous microstructures were observed for films with the lowest and highest agar concentrations. Due to the role played by these biopolymers in the bioplastics industry and biomass processing technology, DES are acknowledged as promising solvents/additives in these areas. Recently, the use of DES as plasticizers for starch and starch-zein blends has been revisited [84]. Combining experimental and numerical studies, the plasticizing ability of five different solvents was ranked – cholimium acetate, glycerol, butyl methyl imidazolium chloride, ChCl/glycerol, and ChCl/urea [84]. Two distinct behaviours were found among the solvents employed, with conventional solvents conferring elastoplastic properties and IL and DES hyperelastic behaviour. Among the studied media, IL and DES resulted in an imperfect interfacial effect, though further studies are needed to unravel the complexity of such processes. Andrade et al. reported the application of ChCl/citric acid eutectic mixtures as plasticizing agents for chitosan films [85]. DES contributed to homogenizing the film-forming dispersion and the film, leading to higher tensile strength and higher storage moduli. Colorimetric tests carried out on the DES-plasticized films revealed significant colour changes, especially at pH > 8. The chitosan films formed are thus sensitive to pH changes and are good candidates to be employed as food indicators.

4.1.3. As monomers

The use of DES as monomers has been reported essentially in two areas: in Molecular Imprinted Technology (MIT) [86–91] and in the preparation of polymeric-based DES [91–95]. The synthesized materials have been mainly employed in extraction, separation and purification technologies.

DES are currently recognized as an excellent and eco-friendly choice to replace conventional solvents in the preparation of molecularly imprinted polymers (MIPs), since these solvents can improve the affinity and selectivity of MIPs to a target molecule, which brings great advantages in separation and purification processes within the framework of green chemistry [90].

Liu et al. [86] synthesized magnetic DES-MIPs using a ChCl/metacrylic acid eutectic mixture as the functional monomer. The analysis of the materials by FTIR, TGA, TEM, SEM, DLS, elemental analysis and VSM revealed that the MIPs were formed effectively and exhibited magnetism (Fig. 5). The DES-MIPs obtained were suc-

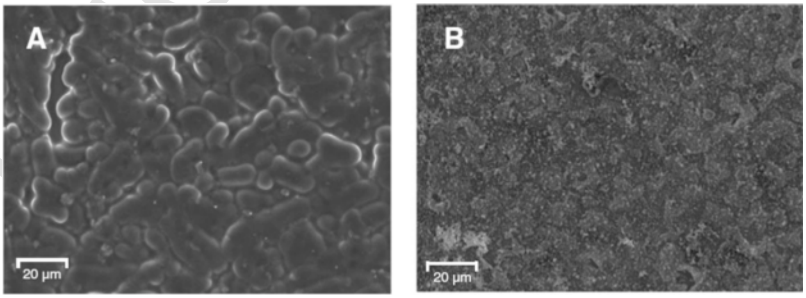

Fig. 4. SEM micrographs of A: PEDOT (ChCl/urea) and B: PEDOT(PSS) on GCE.*From* [76], *reproduced by permission of Elsevier.*

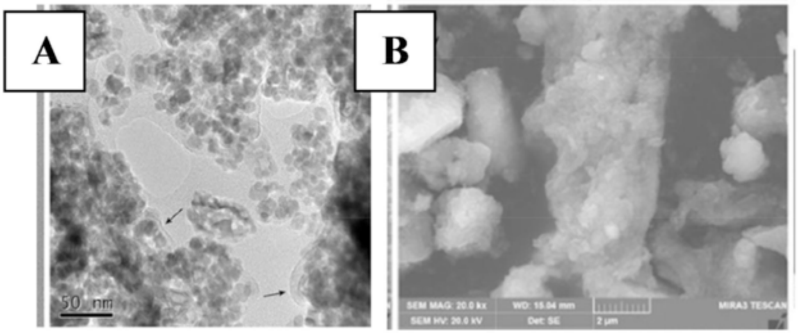

Fig. 5. TEM (A) and SEM (B) images of magnetic DES-MIPs obtained using a ChCl/metacrylic acid eutectic mixture as the functional monomer.*From* [86], *reproduced by permission of Elsevier.*

cessfully applied to the selective recognition and separation of the protein bovine haemoglobin. In [87], a new approach to the purification of complex protein samples was proposed, using ChCl-based DES as auxiliary solvents to modify hybrid MIPs. The materials prepared were characterized by FTIR and SEM, and employed as solid-phase extraction agents for the simultaneous purification of rutin, scoparne and quercetin, showing good performances. In 2017, Li et al. described the modification of MIPs by betaine-based DES [88]. The DES-MIPs were characterized by FESEM and FTIR and adopted as extracting agents for the purification of the antibiotics levofloxacin and tetracycline from the millet extract. The authors underlined the improved molecular recognition ability of the DES-based materials, compared to other MIPs. This feature was also highlighted in [89], reporting better recoveries and purer extracts when a molecular imprinted phloroglucinal-formaldehyde-melamine resin was synthesized in DES and used as a solid-phase extraction sorbent for the selective isolation and recognition of chlorprenaline and bambuterol in urine.

In the last two years, several reports have been published on the use of DES as monomers for the synthesis of DES-based polymers with noteworthy potential advantages in purification processes compared to other materials [91–94]. Poly(DES) grafted silica-coated magnetic microspheres were synthesized by polymerization of a ChCl/itaconic acid eutectic mixture [92] and employed for the magnetic solid-phase extraction of trypsin, with good selectivity and yields. According to the evidence provided by the authors, the microspheres can be recycled six times without significantly losing extraction ability, and can also be used for the purification of the enzyme from crude bovine pancreas extract. Besides biomolecule separation, the application of DES-based polymers has been rapidly spreading to other industrial separation and extraction processes [91,93,94]. For example, polyol-based DES synthesized with the aid of ChCl and glycerol/EG were applied to the removal of lead from contaminated soil [93]. Poly(ionic liquids) prepared using ammonium-based DES monomers revealed strong potential as solid sorbents for CO_2 capture [94], and polyethyleneglycol-based DES were employed for the extractive desulfurization of liquid fuel [91]. Structural characterization studies revealed the integrity of all the materials described.

4.2. Application of DES in metal processing

The deposition of metals and alloys for the industrial coating of surfaces is nowadays a well-established industrial practice, as well as of functionally graded materials [96]. Several processes are used to obtain a variety of electrodeposited coatings with different characteristics and functionalities. There are, however, some important limitations, since not all metal/substrate combinations are possible. These limitations are related to the nature of the electrolytes used for the majority of the metal plating processes, which are water based. Although water has been the most common choice to formulate a plating electrolyte, it presents some inconveniences such as a relatively narrow potential window, reactivity towards specific metals and high hydrogen evolution in specific industrial conditions, which compromises the efficiency of the process. A possible way to overcome these limitations is to extend the range of coating/substrate combinations with the use of non-aqueous solvents, characterized by an extended potential window and improved inertness. DES are a particularly promising class of such systems which have recently been used for metal plating, especially for corrosion protection of less-noble metals, as well as for sensor technology, in combination with other nanomaterials such as polymers and carbon materials. This class of solvents strongly affects the composition and morphology of the deposit, which consequently contributes to an improvement in the electrical, conductivity, and final mechanical properties of the deposits. However, parameters such as the temperature, viscosity, conductivity, and the use of additives [97–101], have to be adjusted for ideal metal electrodeposition when using DES as solvents.

4.2.1. Parameters that influence the electrodeposition of metals

4.2.1.1. Temperature, viscosity, conductivity

The temperature-viscosity dependence of DES has been thoroughly investigated due to its practical and industrial relevance in the electrodeposition of metals and alloys.

Typical DES viscosities are of the order of mPa at around ambient temperatures or slightly higher [102]. The high viscosity of DES is often attributed to the presence of an extensive hydrogen bond network between the two constituents, which results in a lower mobility of free species within the DES solution. Other significant contributions are the large ion size and very small void volume of the majority of DES, as well as electrostatic forces and Van der Waals interactions. Owing to their potential application as green media, the development of DES-based solutions with low viscosity is highly desirable. Besides temperature and viscosity, the eutectic mixtures are also significantly affected by the chemical nature of the DES components [4,103].

The effect of temperature on the electrodeposition of metals in DES media was observed by Ru et al. [104] when they used lead(II) oxide in ChCl/urea DES for the preparation of sub-micrometre lead wires by electrodeposition on stainless steel sheets. The influence of temperature on the lead deposit morphology is depicted in Fig. 6. When the electrodeposition was carried out at 323 K, the lead wires obtained had an average particle size of 2–4 μm in length and 1 μm in diameter. At 343 K, the size of the lead wires increased to 20 μm

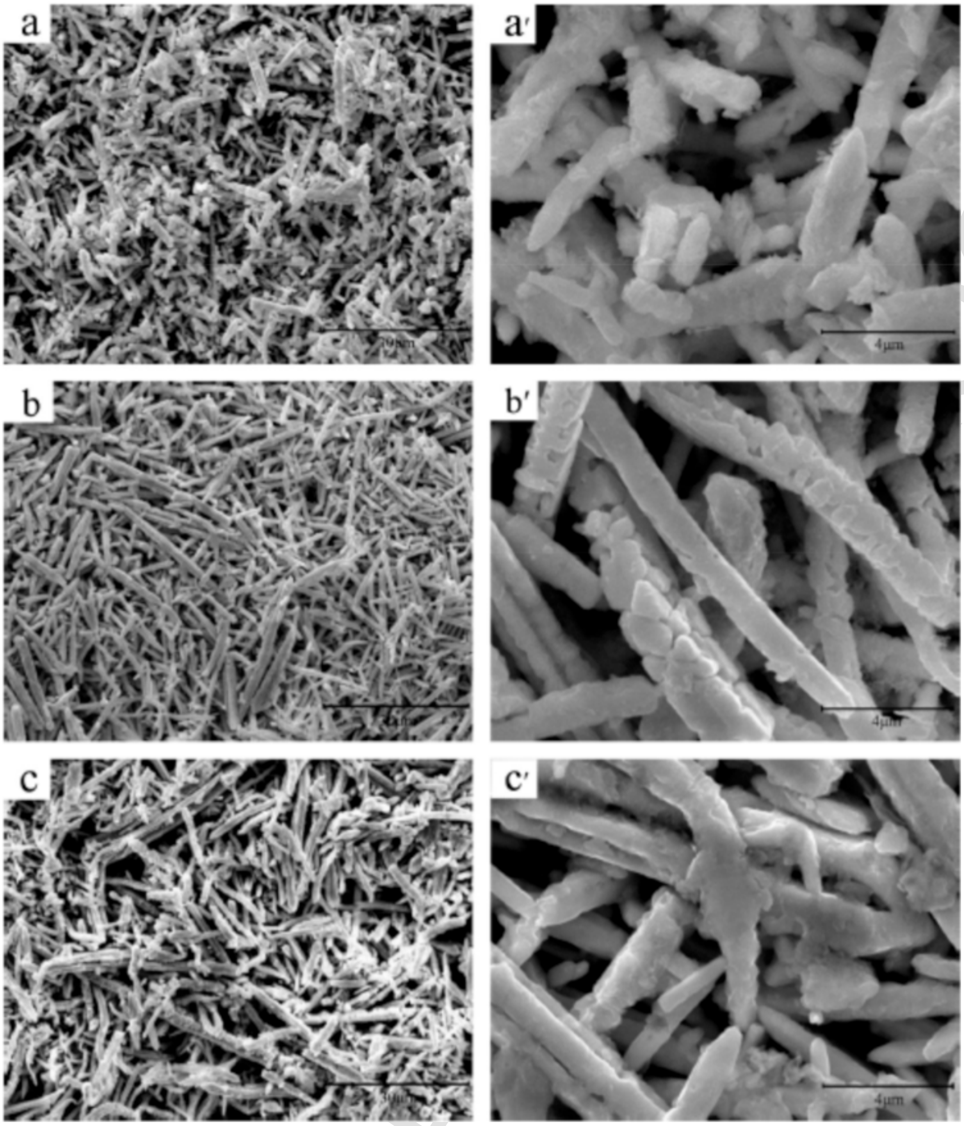

Fig. 6. SEM micrographs of lead deposits at 100 A m^{-2} at different temperatures: (a) 323 K, (b) 333 K, and (c) 343 K. (a′ to c′) are the corresponding magnified SEM images.*From* [104]*, reproduced by permission of Elsevier.*

length and 1.5 μm diameter, indicating that the particle size of the lead powder increases progressively with increasing temperature. The increase of the temperature also led to a decrease of the viscosity, resulting in a significant increase in the electrical conductivity of the ChCl/urea eutectic mixtures. At lower deposition temperatures, due to the high viscosity and low electrical conductivity of the electrolyte, the Pb (II) ion migration rate and the cathodic reaction are very slow, leading to a lower rate of grain growth. In contrast, when the temperature is raised, the Pb (II) ion migration rate speeds up remarkably, in this way favouring a higher nucleation rate and an enhanced grain growth rate at the substrate interface [104–106]. The same tendency was observed by Xie et al. [107], when Zn and Cu–Zn alloys were electrodeposited on copper sheets, using ChCl/urea as media, with temperatures ranging from 313 to 353 K. At higher temperatures, the reaction rate and the growth of nuclei were accelerated with the formation of a thicker layer. Alcanfor et al. [108] electrodeposited indium on copper sheets using a ChCl/EG eutectic mixture as electrolyte. The effect of the temperature was also evaluated in the range from 298 to 338 K and, once again, the increase of temperature contributed to the growth of the nuclei of the metal electrodeposited.

4.2.1.2. Use of additives

The use of additives as co-electrolytes of DES in metal electrodeposition has been explored due to their influence on the growth and structure of the resulting deposits, especially when it is desired to work at room temperature. The presence of additives has been shown to influence the physical and mechanical properties of the deposits such as grain size, brightness, internal stress and even chemical composition [109]. It has been frequently assumed that additives act as catalysts or inhibitors of the electrodeposition by increasing the tendency of metal ions to form complexes and/or raising the activation polarization of single ions by blocking the active sites on substrates. and they can be chosen according to the required final properties of the electrodeposited metals or alloys [110]. The use of additives with DES for improving the electrodeposition of metals and alloys has been extensively described in the literature. For example, ChCl/EG + molecular additives (nicotinic acid, methyl nicotinate, 5,5-dimethylhydantoin and boric acid) were used for nickel electrodeposition [111], ChCl/EG + amine additives (thiourea, ammonia, ethylenediamine) were employed for zinc electrodeposition [112], and a comparative study with different DES (ChCl/EG, ChCl/propylene and ChCl/urea) + chelator additives (EDTA, HEDTA, and Idranal VII) was carried out for zinc–tin electrodeposition [113]. Abbot et al. [111] investigated the influence of molecular additives on the electrodeposition of nickel. In this study, the quantity of material electrodeposited with and without additives was evaluated by electro-gravimetric studies using a quartz crystal microbalance (QCM). It was observed that, with all the additives used, the increase of mass with faradaic charge was approximately linear suggesting that the efficiency of the process remained constant throughout the duration of the experiment. Another relevant aspect is that there were no passivation effects. The use of additives in this system significantly alters the nucleation and growth mechanism of nickel compared to the additive free system. In the same study, morphological aspects were also investigated. All additives used produced bright, mirror-finish, adherent and dense coatings with few identifiable surface features. The enhancement in the properties of the electrodeposited metals and alloys shows the efficiency of the use of additives in the electrodeposition processes.

4.2.1.3. Metal salts

In electroplating processes, the type and concentration of the metal are critical in order to control the morphology and coating rate of the metal deposited. In other words, the coordination chemistry and concentration of the metal complex is the key factor for the design of ionic deposition systems. The most common metals are Cu, Au, Cr, Ni, Ag, Zn, Sn, zinc–tin, zinc–nickel, and nickel–tin alloys [114]. The majority of the investigations have been performed using chlorides and the metal complexes formed between the Lewis acids of the metal and the Lewis base of the DES. DES have a high solubility ability for metal salts, metal oxides and hydroxides. This unusual property gives these solvents a big advantage over aqueous and organic based electrolytes. It also means that passivation processes are not observed when DES are used and which permits the formation of thicker metal films [115]. On the other hand, in aqueous solution, the effect of passivation is frequently observed due to the formation of non-soluble oxide and/or hydroxide on the surface of the electrode. Although it is rather difficult to compete economically with the existing plating processes for metal deposition applied in industry for corrosion protection, DES media are nowadays a promising alternative that can provide a suitable, economic and environmentally friendly medium for industrial applications involving electroplating technology [6].

Some of the common metals and alloys electroplated using DES as solvent are summarized below.

4.2.1.3.1. Nickel

Bernasconi et al. [116] studied the possibility of nickel deposition from ChCl/urea on aluminium, which is a water sensitive substrate, with the addition of nickel chloride as source of nickel ion and the complexing agent ethylenediamine (ED). Analysis by SEM of the nickel coating revealed a compact, uniform, and adherent coating. From the electrochemical point of view, the results obtained from voltammetric studies showed a clear nickel reduction peak. The presence of ED shifted this reduction peak to more negative potentials, as expected when adding a complexing agent. Furthermore, the possibility to deposit multilayers of nickel in DES was also demonstrated.

4.2.1.3.2. Copper

Since Cu electrodeposition is very common in the surface-finishing industry, many studies involving DES-based copper plating have been done. Gum et al. [117] reported a comparative study in which Cu films were electrodeposited from a base electrolyte composed of $CuCl_2 \cdot 2H_2O$ in ChCl/EG, in the absence and presence of the additive ethylene diamine (EDA). All the electrodeposited Cu films were composed of pure Cu and had an fcc crystal structure, as revealed by EDS and XRD analysis, respectively. Potentiodynamic polarization measurements and SEM studies performed on the corroded surfaces indicated that the addition of EDA to the base electrolyte had a positive effect on enhancing the corrosion resistance of Cu deposits. Mandroyan et al. [118] studied the reduction of copper in the presence of ChCl/EG and assessed the influence of temperature and of ultrasound on kinetic parameters. Temperature increase and ultrasound presented the same effect on mass transfer for reduction of Cu^{II}/Cu^{I}, the standard rate constant improvement being of the same order. By optimization of experimental conditions combining high temperature and ultrasound, plating currents were increased by a factor of 10.

4.2.1.3.3. Zinc

Due to its low cost and corrosion protection ability, zinc has great importance in the metal finishing industry. Several studies have been performed using different DES as alternatives to aqueous solution, in particular, ChCl/EG and ChCl/urea eutectic mixtures. In this context, Yang et al. [96] investigated the electrochemical reduction of zinc oxide to Zn in 1:2 ChCl/urea electrolyte on copper substrates. The solubility of ZnO in the eutectic mixture was investigated by FTIR spectroscopy, and the solubilization temperature was optimized. Optimum values found for the experimental temperature and ZnO concentrations were 373 K and 1.23 M respectively. The nucleation was modelled as an instantaneous process and the growth of the Zn particles was found to be governed by a diffusion-controlled mechanism. The Zn electrodeposited on Cu was characterized by XRD and EDS, revealing highly pure Zn deposits. SEM images showed a transition image in the surface morphology of Zn deposits, from small hexagonal crystals to agglomerated platelets, upon application of higher potentials [119].

4.2.1.3.4. Aluminium

Aluminium is one of the metals that cannot be plated in aqueous solution media because of its electrode potential, which is well below the water decomposition potential. Moreover, although the high stability of aluminium oxides makes the deposits highly resistant to corrosion, it is the main reason for not being able to carry out its electrodeposition. The search for new strategies for the electroplating of aluminium is an important research field for technological applications such as energy storage and anti-corrosion coatings [120]. Recently, the use of DES has allowed the aqueous solution electroplating difficulties to be overcome. Aluminium deposition has been done using type I eutectic mixtures ($Cat^+X^-\ zMCl_x^-$), but the anodic reaction is very slow and rate limiting. Thus, the use of a type IV eutectic mixture ($MCl_x + RZ = MCl_{x-1}^+ \cdot RZ + MCl_{x+1}$), see Table 1, has also been investigated and it has been demonstrated that it is not necessary to have quarternary ammonium cations for Al plating. Although the anodic reaction is still slow and needs to be further investigated to increase the deposition rate, the simple addition of acetamide to $AlCl_3$ seems to lead to electrolytes that favour Al electrodeposition, relatively insensitive to water. Characterization of the liquid phase showed the presence of both anionic and cationic aluminium species, namely $[AlCl_2.\ urea]^+$ and $[AlCl_4]^-$ [6,121,122].

4.2.1.3.5. *Alloys*

Electrodeposition of alloys is important since alloys usually possess properties superior to those of single metals [123]. Electrodeposited alloys can be more corrosion resistant and have better catalytic and magnetic properties. The interest in the electrodeposition of alloys is increasing, especially because the number of alloy combinations is vast. The deposition processes are similar to those of pure metals, and the physical and chemical characteristics depend on experimental factors such as plating bath composition, current density, overpotential, and temperature. In addition, the application of pulsed electrodeposition enables control of the grain size and composition of the deposits [6,124–126]. Furthermore, the electrodeposition of alloys in aprotic liquids such as DES can avoid the limited potential window and hydrogen evolution. Thus, the number of possible metallic element combinations is hugely increased [125]. Several alloy combinations have been prepared in DES-based solvents, summarized in Table 3. As can be seen, the main applications have been as coatings for protection against corrosion. The promising properties of these materials have also led to their application in other research fields such as the fabrication of semiconductors for use in printed circuit boards, and in sensors and biosensors in combination with other nanomaterials.

4.2.2. *Electroless deposition*

The electroless deposition process is an autocatalytic method in which the reduction of the metallic ions in the solution and the film deposition can be carried out through oxidation of a chemical compound present in the solution. The process requires that the cation of the metal to be deposited is reduced by receiving electrons from the surface of a metal substrate or from the surface of the catalyst used to initiate the deposition. The reductant, in turn, delivers electrons to this surface and is thereby oxidized [134]. Electroless plating has comparable characteristics to the electroplating technique in terms of the quality of the material deposited, but improved physical and mechanical properties, brightness and thickness. The desired properties can be attained by choosing the pH, temperature, viscosity, and composition of the bath. Electroless deposition using nickel for coating has assumed the greatest commercial importance among the electroless coatings, including electroless processes in DES [134,135]. Ali et al. [135] carried out a comparative study in which nickel was deposited from nickel chloride on copper and steel substrates, using the electroless and the electrolytic method in either 1:2 ChCl/EG or 1:2 ChCl/urea based DES. The electroless deposition was carried out from the EG and urea based DES containing various concentrations of $NiCl_2$. H_2O, at temperatures ranging from 30 °C to 100 °C. The deposition of nickel from EG-based DES by the electroless method was only possible above 70 °C, and nickel deposits could not be obtained from 1:2 ChCl/urea based DES at any temperature (in the case of electrolytic deposition, nickel was electrodeposited successfully in both EG and urea based DES at temperatures ranging from 30 °C to 70 °C). For the electroless method, all nickel coatings are smooth, shiny and dense with good adherence and with bright metallic coloured nickel. SEM images revealed no significant differences between electroless and electrodeposited thin films. It was difficult to obtain a thick coating in the electroless method, whereas the thickness and the crystal size of the coatings can be controlled using electrodeposition. Abbott et al. [136] demonstrated that sustained deposition of metallic silver can be deposited by electroless on copper substrates using solutions of Ag^+ ions in ChCl/ethylene glycol eutectic mixtures. This work was the first example of the sustained galvanic coating of Ag metal by deposition on a Cu surface from DES. The reduction of Ag^+ in DES was driven by the difference in the Ag^+/Cu^+ redox potentials. It was possible to obtain thick Ag deposits from DES because the deposit was porous and Cu^+ could diffuse away from the substrate, in a process facilitated by the pores and channels present in the Ag deposit. This was observed using both SEM and AFM imaging techniques and QCM studies. Adhesion of Ag deposits was sufficient to be used as coating for preventing corrosion.

There is still not much scientific work published in this area, and further studies can be expected.

Table 3
Alloys prepared in DES-based solvents, ratio ChCl/HBD 1:2.

Alloy	DES	Substrate	Ref.
Ni–Cu	ChCl/ethylene glycol	Copper foil	[127]
Co–Cr	ChCl/ethylene glycol	Mild steel sheets	[128]
Ni–Co–Sn	ChCl/urea	Copper foil	[99]
Ni–Mo and Co–Mo	ChCl/urea	Copper foil	[129]
Ni–Sn	ChCl/ethylene glycol and ChCl/maleic acid	Copper foil and mild steel sheets	[100]
Zn–Co	ChCl/urea	Copper foil	[130]
Ni–Zn	ChCl/urea	Copper foil	[131]
Cu–In	ChCl/urea	Molybdenium sheets	[132]
Cu–Sn	ChCl/urea	Platinum sheets	[133]

4.2.3. *Characterization of the electrodeposited films*

The metal and alloy films prepared by electrodeposition methods using DES have been characterized in terms of corrosion resistance in aggressive media, crystal size, morphology, elemental composition and electrochemical behaviour. In addition, a variety of important properties such as magnetism, resistance, thickness, and others, which might be relevant for applications in aerospace, electronics, energy, medicine, etc., have been described.

4.2.3.1. *Voltammetric studies*

Cyclic voltammetry has been employed to acquire information about the electrochemical behaviour of DES with and without the electrodeposited metal species at different scan rates, metal concentrations and temperatures, and also to investigate the electrodeposition mechanisms. Bernasconi et al. [137] studied the electrochemical behaviour of $CuSO_4$ in ChCl/EG at different scan rates using cyclic voltammetry, and concluded that the reduction process occurs in two steps. The first reduction reaction ($Cu^{2+} + e^- \rightarrow Cu^+$) is observed around 0.2 V, while the second ($Cu^+ + e^- \rightarrow Cu^0$) is around −0.75 V.

Sebastián et al. [138] investigated copper electrodeposition on Au(poly) and on Au(*hkl*) single crystals, using ChCl/urea mixtures. The voltammetric profiles of the copper electrodeposited on Au(poly) showed a sharp oxidation peak on the reverse scan (Fig. 7A and B), indicating easy dissolution of the copper deposit. The authors suggested that the presence of a high chloride concentration in the DES favours the process. The copper electrodeposition results obtained showed that DES mixtures affect the final structure of the underpotential adlayers because the chloride ions of DES lie on the top of the copper adlayer, which shifts the peak potentials and changes the kinetics; there can also be effects from other species in the DES mixtures.

Chronoamperometry experiments have been used in metal electrodeposition in order to obtain information about the electrodeposition mechanisms. Salomé et al. [139] studied Sn electrodeposition in various DES mixtures (ChCl/urea, ChCl/EG and ChCl/propylene glycol), at 75 °C and at different potentials. Chronoamperograms showed the typical behaviour usually observed for metal deposition. The change of the hydrogen bond donor of the eutectic mixture (urea,

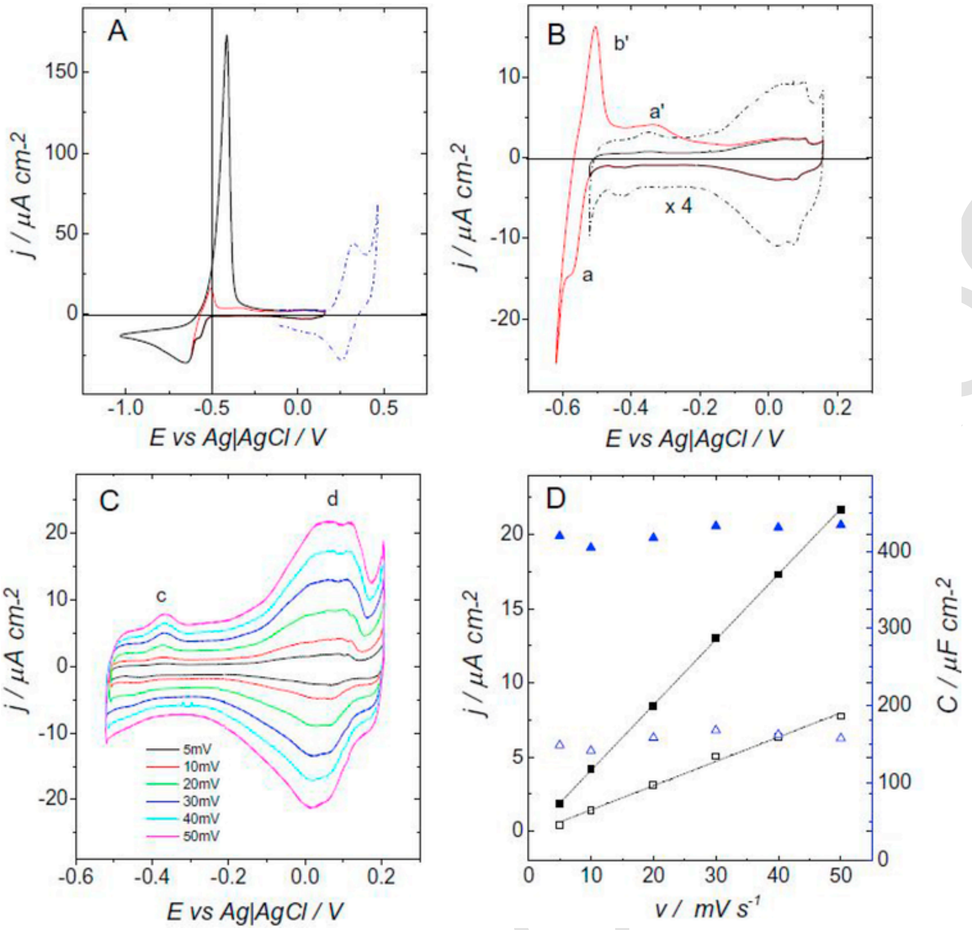

Fig. 7. Cyclic voltammograms for copper electrodeposition on Au(poly) from a 10 mM CuCl + DES solution: (A) and (B) different potential limits (dashed line in B is just an enlargement of the black curve). Scan rate at 5 mV/s. (C) Copper UPD recorded at different scan rates. (D) Plots of current densities (squares) and pseudocapacitance (*j*/*v*) (triangles) of the UPD region vs the scan rate. Open and filled symbols correspond to the maximum values measured at peaks c and d, respectively, from (C). The vertical line in (A) marks the reversible potential for bulk copper deposition.*From* [138], *reproduced by permission of Elsevier*.

ethylene glycol or propylene glycol) did not affect the voltammetric profile. However, the time for overlapping of diffusion layers was found to be significantly higher for ChCl/urea mixtures than for ChCl/propylene and ChCl/EG. The measured nucleation rates strongly indicated that the important role of the DES on the nucleation and growth processes can be attributed to the viscosity.

4.2.3.2. Corrosion studies

Corrosion tests have been the most frequently employed technique for the characterization of the electrodeposited films prepared in DES. Polarization curves and electrochemical impedance spectroscopy (EIS) have been extensively used to characterize the films in terms of corrosion resistance in aggressive media (e.g. NaCl, KOH).

Potentiodynamic polarization studies have been used to compare the corrosion resistance of metal alloy films prepared in DES mixtures. Vijayakumar et al. [99] demonstrated that the ternary alloy film Ni–Co–Sn prepared in ChCl/EG, showed a better corrosion resistance than the binary alloy films Ni–Sn and Co–Sn. The corrosion resistance reflects the surface morphology. SEM images revealed that Ni–Co–Sn and Ni–Sn alloys had almost the same morphology, but polarization studies showed that the ternary alloy was more stable in alkaline solution.

Anicai et al. [100] compared the corrosion behaviour of Sn and Ni-Sn alloys films prepared in DES mixtures and in aqueous electrolytes by EIS and potentiodynamic polarization studies in 0.5 M NaCl and for various immersion periods. The polarization curves and the electrochemical impedance spectra, recorded for immersion periods up to 48 h, showed that the Sn films prepared in ChCl/malonic acid had a better corrosion performance, without surface modifications, than Sn coatings obtained in aqueous electrolytes. Polarization curves for the Ni–Sn alloy film prepared in ChCl/EG, showed that the corrosion potential did not change, but a decrease in corrosion current after 336 h of immersion suggests the formation of a protective thin passive film, in agreement with previous studies [140,141]. Furthermore, and according to the morphology studies performed, it was suggested that these results are related to the fact the deposit is compact with a nanocrystalline structure, which could avoid the penetration of chloride ions.

4.2.3.3. Morphological and chemical analysis

The metal and alloy deposits prepared in DES, have also been characterized by advanced analysis techniques, which can give information about the surface morphology, crystalline structure, chemical composition, topography profile, etc. Li et al. [142] studied cobalt electrodeposits prepared in ChCl/urea mixtures, at different operating temperatures by SEM, EDS and XRD. The results (Fig. 8) evidenced uniform, dense, compact and high Co content films at low temperatures and at less negative potentials. At higher temperatures, the

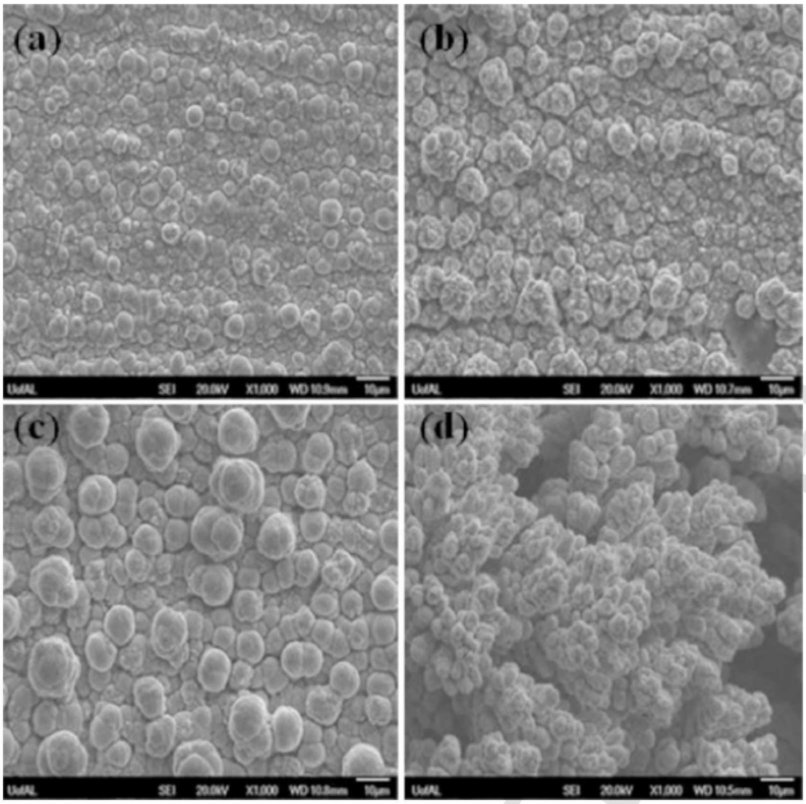

Fig. 8. SEM micrographs of cobalt electrodeposits obtained from urea-choline chloride-$CoCl_2$ (0.05 mol L^{-1}) on a copper substrate at different potentials: (a) −0.80 V, (b) −0.85 V, (c) −0.90 V, and (d) −0.95 V at 373 K.*Adapted from Ref.* [142]*, reproduced by permission of Elsevier.*

cobalt electrodeposits tended to form cauliflower structures with different sizes.

Morphological analysis was also used on copper electrodeposits prepared using DES and aqueous solutions. Sebastián et al. [143] prepared copper deposits in ChCl/urea and compared them with those prepared in aqueous media (NaCl and $NaClO_4$). The SEM images of copper deposits made in DES (Fig. 9A and B) showed that the small grains formed when applying low overpotentials make the nucleation and diffusion processes difficult. Increasing the overpotential and charge, grains appeared with similar morphology. In the case of copper deposits prepared in aqueous solution (Fig. 9C), blocks or crystals of large size were formed. The SEM images of copper deposits prepared with in DES and aqueous solution showed grains of different sizes but similar morphology, which indicates that the medium does not affect the morphology. The authors also investigated the effect of chloride ion by preparing copper deposits in $NaClO_4$ at different potentials (Fig. 9D and E), concluding that electrodeposition is faster in perchlorate than in chloride medium. The results confirmed a slower diffusion process in the case of the copper deposits from DES than in aqueous medium, which results in a homogeneous distribution of grains of smaller size.

Atomic force microscopy (AFM) has been used to study carbon nanotubes coated with chromium based DES mixtures, providing information about the topography and magnetization profile of these films. Wright et al. [144] successfully deposited nanomagnetic domains of chromium on vertically aligned CNT with DES solutions (ChCl/chromium (II) chloride), a process that it was not possible to do with aqueous solutions. The magnetic force images obtained (Fig. 10d) suggested the presence of small chromium clusters when thin films were deposited; on the contrary, thicker films with no magnetic character were observed (Fig. 10f). According to theoretical work, the reason why no magnetic profile was visible, was because bulk chromium is an itinerant antiferromagnet, but small clusters of chromium exhibit a strong magnetic moment.

4.2.3.4. Mechanical and physical properties

The mechanical and physical properties of the electrodeposited films in terms of hardness, thickness and friction have also been evaluated. The hardness of Ni films prepared with ChCl/EG mixtures was compared with those prepared in aqueous solutions by measuring the resistance to indentation. Abbott et al. [98] observed that the use of DES mixtures in nickel electrodeposition increased the coating hardness. SEM indicated that a dense and uniform Ni deposit was formed when using ChCl/EG, while a dull and rough deposit was formed in aqueous media.

4.2.4. Applications of films prepared in DES

The combination of metal electrodeposition processes and DES has been extensively explored by researchers. The films and/or coatings prepared and reported have as their main purpose the protection of other materials from corrosion. According to the literature, these materials can be applied in industries such as automotive, aerospace, electronics and medicine.

ChCl/EG eutectic mixtures at 1:2 mole ratio were used to prepare Ni–Co alloy films by a simple electrodeposition process at room temperature [145]. These films have been extensively applied as engineering materials because of their interesting properties such as high strength, good corrosion resistance, heat-conductive and electrocatalytic activity [145]. Wang et al. [127] successfully prepared Ni–Cu alloy films in 1:2 ChCl/urea mixtures, without the need of additives.

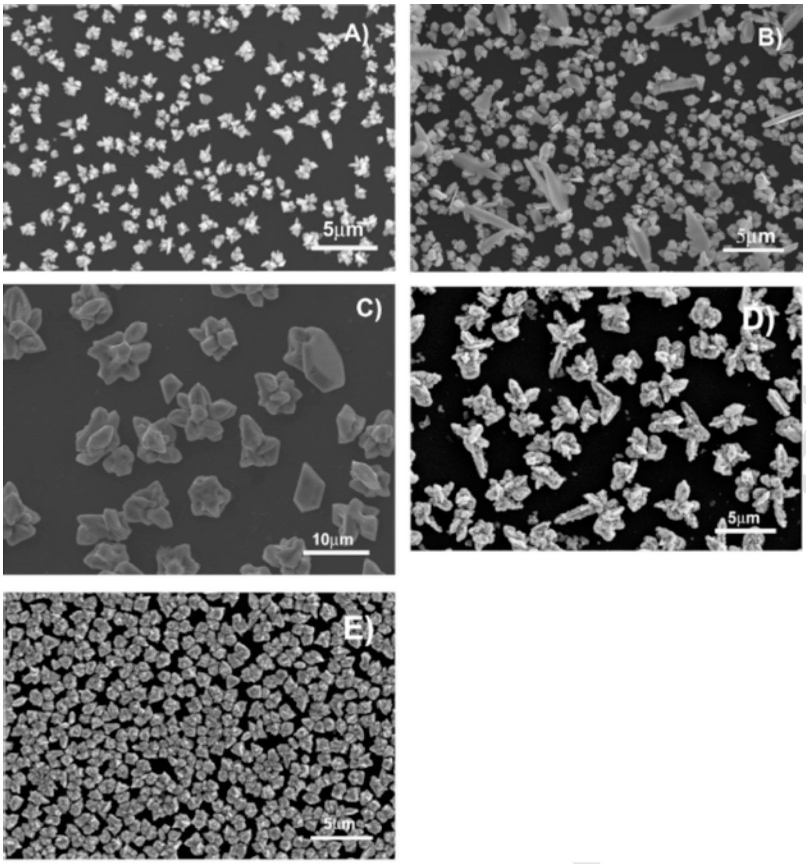

Fig. 9. SEM images of deposits prepared potentiostatically from different solutions: 0.05 M CuCl in DES solvent at: (A) −850 mV, $Q = -10$ mC and (B) −870 mV, $Q = -30$ mC; (C) 0.01 M CuCl + NaCl 3 M solution at −300 mV, $Q = 20$ mC, and 0.01 M CuCl + 0.6 M $NaClO_4$ solution at: (D) −100 mV, $Q = -15$ mC and (E) −115 mV, $Q = -15$ mC.*From* [143]*, reproduced by permission of Elsevier.*

These films, which are also used as engineering materials, presented superior corrosion resistance than the Ni–Cu films obtained from aqueous plating electrolyte.

ChCl/EG eutectic mixtures at 1:2 mole ratio were also used for the preparation of ternary Ni–Co–Sn alloy films, which exhibited better electrocatalytic activity and higher stability in alkaline solution than the binary alloys Ni–Sn and Co–Sn, and were demonstrated to be good candidates for the hydrogen evolution reaction and as anode materials for lithium batteries [99].

Other binary systems prepared from deep eutectic mixtures are Cu–Sn alloy films, which are important for corrosion protection, shape memory applications and lithium ion batteries [146]; Zn–Sn alloy coatings, which can be applied in various industries as alternative to toxic cadmium and allergenic nickel, and for corrosion protection of steel [147]; Fe–Ga and Co–Pt films, which have interest to be used in micro- and nano-electromechanical and on magnetostrictive devices because of their magnetic properties [148,149]; Ni–Sn alloy coatings, which have a good corrosion protection and can be useful in printed circuit boards and as an alternative to Cr coatings [100].

Besides binary and ternary alloys, metal and metal alloys have been electrodeposited from DES, for example, Zn films on dense alumina layers for the preparation of 1-D nanostructures to be applied on semiconductors [150]. In and its alloys were prepared for the same purpose, to be used in electronic and optoelectronic devices [108].

ChCl/EG mixtures were also used as medium to prepare nanocomposite coatings by electrodeposition such as metal matrix composite coatings of Ni/SiO_2 [151]. These materials are known for their excellent corrosion resistance, wear resistance and other advantageous properties. Species other than SiO_2 have been used, including SiC, graphene oxide, PTFE, Al_2O_3 and CNT [151].

DES have been employed as deposition media to improve electroless processes. Kang et al. [152] presented a novel and simple approach to a fast electroless Ni-P process on Al alloys at medium-low temperatures, which normally requires temperatures above 80 °C to achieve a good deposition rate. They found that a Cu immersion pre-treatment on Al alloys in ChCl/EG mixtures, through a galvanic replacement deposition, leads to an improvement of the deposition rate of electroless Ni–P process over a wide range of temperatures, without the need for additives or application of external energy. Electroless Ni–P coatings have attracted great interest in various industries (such as automotive, aerospace, electronics, chemical process, tooling, printing, etc.) mainly because of their high hardness and solderability, as well as corrosion and wear resistance.

4.3. Application of DES in nanomaterials science

In the last decade, DES has had a large impact on nanomaterials science and have established themselves as one of the leading new choices for application in nanotechnology.

The use of DES in nanoscience was first introduced in 2008, when Sun et al. reported the DES-assisted synthesis of pentacle gold nanocrystals in ChCl/urea eutectic mixtures [153]. Since then, many applications of DES in nanotechnology through many approaches have been published. DES have been mainly used as reaction media

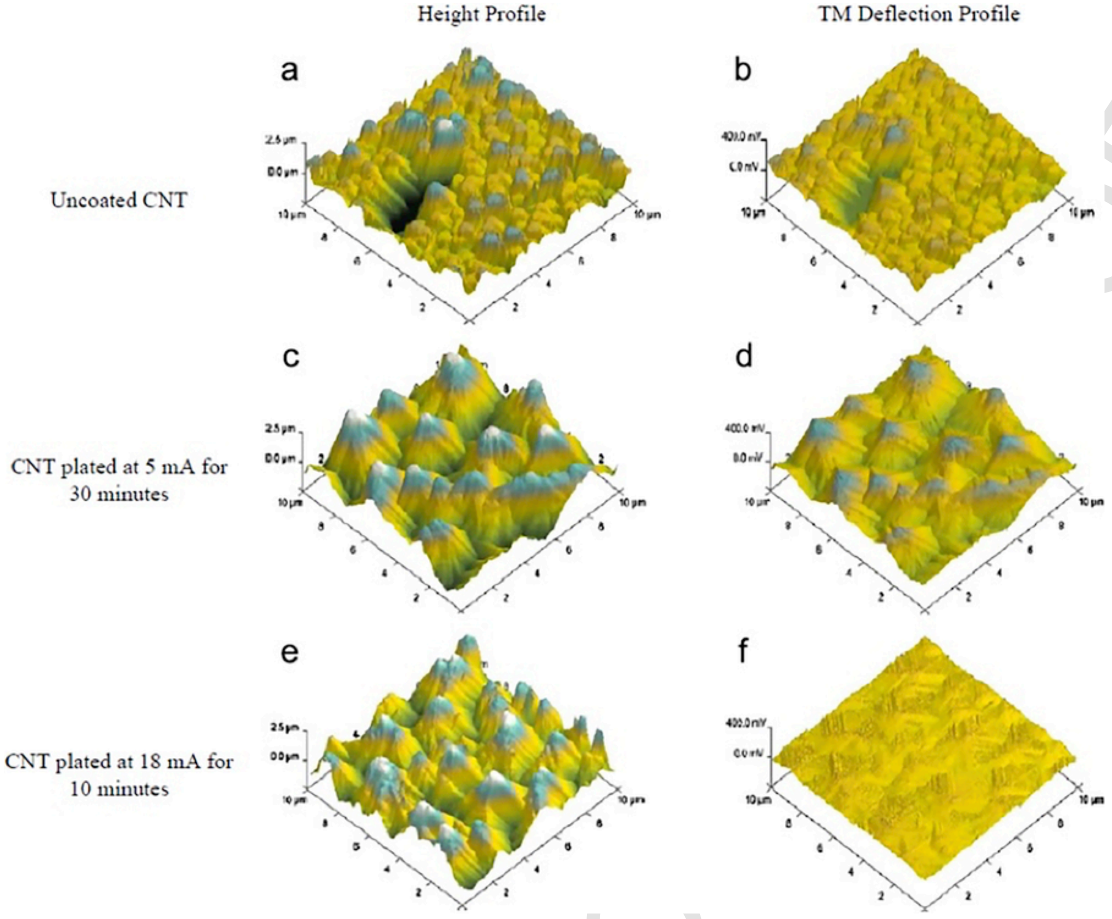

Fig. 10. AFM topography of uncoated and chrome coated CNTs together with the magnetization profile of the same area. Uncoated nanotubes are shown in (a) topography and (b) magnetic profile. Nanotubes electroplated at 5 mA for 30 min are shown in (c) topography and (d) magnetic profile. Deposits created using higher currents (18 mA) for shorter times (10 min) are shown in (e) topography and (f) magnetic profile.*From* [144], *reproduced by permission of Elsevier.*

for the synthesis of nanomaterials and for nanomaterial electrodeposition, and as media to disperse nanoparticles and control morphology in order to obtain the desired products with a defined morphology or chemical composition. Amongst the various nanomaterials prepared in DES, carbon nanomaterials have been the most popular, followed by metal oxide and gold nanoparticles. More recently, new materials and biomaterials are being produced such as inorganic (bio)nanomaterials and metal (bio)organic framework materials. ChCl/urea eutectic mixtures have been by far the type of DES most employed. Details on the use of DES in nanotechnology up until 2015 are available in an excellent review [7]. The work reviewed here will concentrate on more recent publications.

4.3.1. As reaction media for the synthesis of nanomaterials

A large number of nanostructured materials has been synthesized using DES as solvents and reactants. In the fabrication of nanomaterials, DES have been also used as precursors, templates and dispersants to modulate nucleation and growth mechanisms, functioning as designer solvents to influence the size and morphology of nanomaterials.

In the last two years, new attempts have been made towards the development of simple, green, affordable and sustainable DES-based methods for the production of inorganic nanomaterials with important applications. Calcium phosphate, hydroxyapatite and fluorapatite are compounds largely employed in the medical area, for dentistry and orthopaedic purposes. Karimi et al. [154] described the preparation of calcium phosphate nanoparticles in ChCl/urea eutectic mixtures. The role of the synthesis temperature on the structural properties of the products obtained was assessed. The analysis of the materials by X-ray diffractometry, FESEM, X-ray spectroscopy and FTIR showed that, in the presence of DES, the crystallinity and particle size were temperature dependent. The DES-assisted synthesis method was considered as a novel green route for the fabrication of nanobiomaterials. In 2017 [155], the same authors performed additional studies on the same system, further evaluating the effect of synthesis time and temperature on the crystallinity, properties and elemental purity of the calcium phosphate nanoparticles synthesized. X-ray diffraction, FESEM, X-ray spectroscopy and FTIR techniques revealed the formation of amorphous calcium phosphate nanoparticles with spherical morphology and high elemental/structural purity. Nanocrystalline hydroxyapatite powders [156] were prepared by a simple and sustainable method using ChCl/urea as solvent. Characterization of the materials confirmed the production of high purity nanosized, crystalline hydroxyapatite powders (Fig. 11). Recently, a simple, fast, low cost and sustainable method was proposed for the synthesis of fluorapatite nanoparticles [157]. The ChCl/urea eutectic mixtures used as solvents controlled the particle size, as well as leading to crystalline, elementally and structurally highly pure products with good biocompatibility, osteogenity and mineralization ability, besides the possibility of a successful recovery of the solvent.

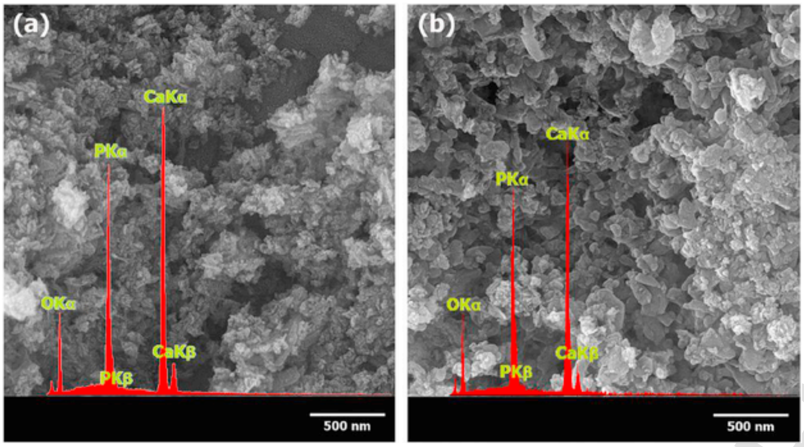

Fig. 11. FESEM micrographs of hydroxyapatite powders prepared by a simple and sustainable method using ChCl/urea as solvent, and two different sets of experimental conditions, (a) and (b). The insets show EDS patterns.*From* [156]*, reproduced by permission of Elsevier.*

Using DES to enhance the catalytic properties of nanomaterials through the control of their composition, surface structure and morphology has also been explored. Nickel/nickel nitride nanocomposites [158] with different compositions and morphologies, and attractive catalytic performance, were prepared employing a ChCl/urea-assisted method. ZnO nanoparticles [159] were synthesized by a ionothermal precipitation method in ChCl/EG. XRD, SEM, FTIR, XPS, TGA, UV–vis and photoluminescence (PL) spectroscopic studies performed on the nanomaterials showed the presence of stable and uniform ZnO nanoparticles, with improved dispersion stability and catalytic performance. In [160], a novel oxidative precipitation-combined ionothermal method for the synthesis of Fe_3O_4 magnetic nanoparticles is presented. The nanomaterials produced were stable and showed a superior catalytic efficiency for the degradation of organic pollutants in water treatment. Anicai et al. [161] reported the electrochemical synthesis of high quality TiO_2 nanopowders in ChCl/EG or urea DES, a nanomaterial which is widely used in industrial applications such as solar cells, photocatalysis, chemical sensors, microelectronics and electrochemistry. Gold nanofoams were prepared on zinc substrates [162] in ChCl/EG without the aid of any templates, seeds or additives; they exhibited exceptional catalytic efficiency for the reduction of aromatic nitrocompounds.

Another very popular research area has been the optical and energy storage field. For example, lead sulfide (PbS) nano-/micro-rod-based thin films [163] were synthesized by a simple and economic ionothermal method, using ChCl/urea DES. Highly (200)-oriented shuttle like PbS thin films were obtained, with large absorbance and a broad emission band, with potential application in solar cells. Zhang et al. [164] described the fabrication of chalcopyrite structured copper indium disulfide ($CuInS_2$) nanorods via a microwave heating method, in ChCl/urea (Fig. 12). Analysis of the optical properties of the nano-

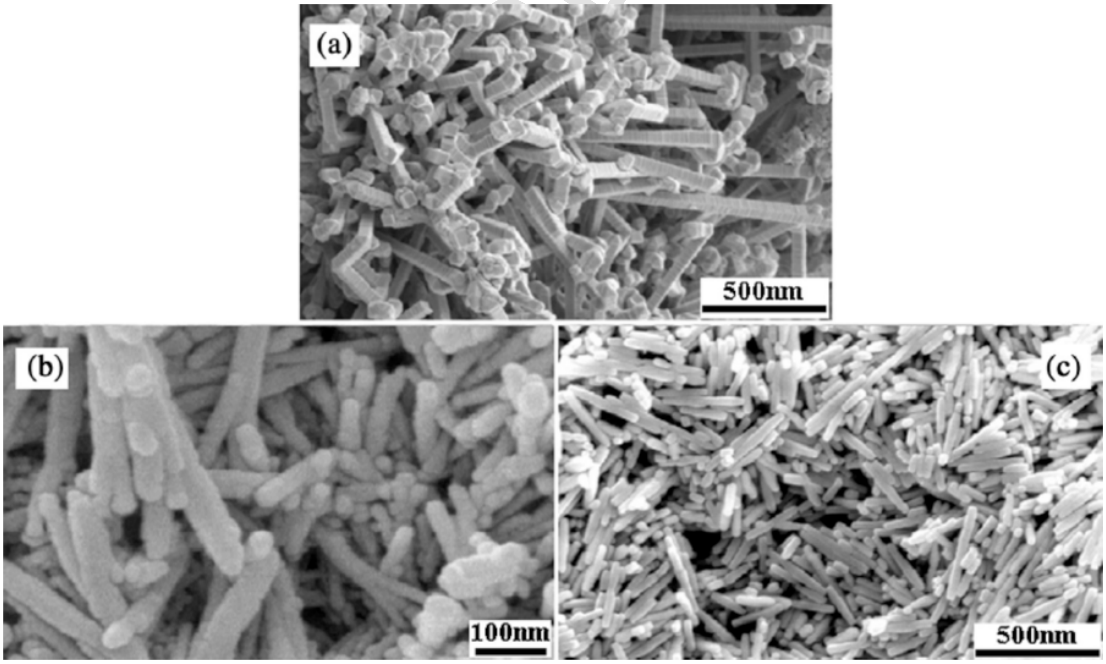

Fig. 12. SEM images (a–c) of the $CuInS_2$ nanorods prepared by microwave heating method in different reaction times: (a) 10 min, (b) 15 min, and (c) 20 min.*From* [164]*, reproduced by permission of Elsevier.*

materials by UV–vis and PL spectroscopy revealed strong absorption over the whole visible light region to the near IR, suggesting promising applications in light emitting diodes, photovoltaic cells and optical devices. In [165], a ionothermal method employing ChCl/urea as reaction media was proposed for the preparation of Fe_2O_3 nanospindles, with high storage capacity and good cycling ability as anode material for use in lithium ion batteries. Copper-zinc-tin chalcogenide, a very attractive semiconductor in photovoltaic devices, was synthesized via an easy, low-cost and sustainable method using ChCl/urea both as solvent and template [166]. Silver nanoparticle colloidal suspensions [167] were produced in a ChCl/urea eutectic mixture by using laser ablation targeting a silver metal blank immersed in the DES. The luminescent properties of the silver nanoparticles were found to be better than those obtained in aqueous solutions.

Other versatile inorganic nanomaterials with diverse applications have also been prepared using DES. In [168], the synthesis of nickel nanostructures performed on a copper-based template in a ChCl/EG eutectic mixture, by a galvanic replacement reaction, was described with different morphologies from those obtained in conventional solutions. Recently, studies on the ionothermal synthesis of ultrathin Mg–Al layered double hydroxide in ChCl/urea [169], led to crystalline layered structures composed of monolayer nanosheets. The potential application of these nanomaterials for the removal of borate in phosphorization wastewater was indicated. In 2017, Karimi et al. investigated the ternary role of DES – reactant, solvent and template – as medium for the synthesis of monetite nanoparticles [170] and Mn_3O_4 nanoparticles [171] using, respectively, $ChCl/CaCl_2{\cdot}6H_2O$ and ChCl-EG eutectic mixtures.

The possibility of applying amyloid fibrils in nanofiber-based materials, biosensors, bioactive membranes and tissue engineering has been lately a topic of research interest. Silva et al. [172] explored the role of DES in the fabrication of protein nanofibres. To this end, they developed a novel and faster fibrillation method for the preparation of lysozyme nanofibres, using a ChCl/acetic acid eutectic mixture as a promotor of hen egg white lysozyme fibrillation. This work could lead to a new route for amyloid fibre production.

4.3.2. As reaction media for nanomaterial electrodeposition

Nanoparticle electrodeposition is currently recognized as a facile, scalable and economic approach to produce supported nanoparticles with important applications. Moreover, the use of electrodeposition methods employing DES as electrolytes offers additional advantages such as more homogeneous distribution of particles, along with rapid deposition rates and reduced amount of waste materials.

Bozzini et al. [173] reported the electrochemical synthesis of nanoporous gold decorated with manganese oxide nanowires, with interesting applications in supercapacitor technology. The Au–Mn surfaces were electrodeposited from a ChCl/urea-based bath and their composition and structure were examined by Raman and SFG spectroscopy, revealing excellent capacitive properties. Porous Ni–Cu alloy nanosheets were directly prepared on copper substrates [174] using a simple potentiostatic electrodeposition method from a ChCl/EG eutectic mixture. The Ni–Cu films obtained showed enhanced catalytic activity for hydrogen evolution, and the DES-based experimental approach was found to be more advantageous and efficient than in aqueous media. In [151], the electrodeposition of homogeneous Ni/SO_2 nanocomposite coatings employing ChCl/EG as electrolyte is reported. The Ni matrix composite coating with uniformly distributed SiO_2 nanoparticles exhibited excellent corrosion resistance. It was also proved that the DES can efficiently decrease the agglomeration of the nanoparticles in the electrodeposition bath and enhance their content in the nickel metal matrix, compared to aqueous solutions. Recently, deeper investigations on Pb nanoparticle electrodeposition using DES were carried out [175]. Particle formation, aggregation, coalescence, size, shape and capacitance in a ChCl/urea DES were assessed by X-ray scattering and electrochemical methods, showing distinctive nanoparticle capacitance, mobility and ion mobility.

4.3.3. As functionalization agents

The use of DES as functionalization agents has also been described, the majority of the publications being focused on the functionalization of carbon nanotubes. As is well known, CNT are amongst the most widely used nanomaterials. Despite their potentialities, significant issues concerning the application of CNT have been pointed out, especially linked to dispersability, aggregation and manipulation, as well as the environmentally unfriendly chemicals typically employed for their functionalization. To overcome these problems, DES have been proposed and explored as functionalization agents. Alomar et al. carried out a sequence of investigations on the use of DES for CNT functionalization, with the final aim of forming new adsorbents for the removal of heavy metal contaminants in water treatment procedures [176–178]. In [176], CNT surfaces were functionalized with glycerol/methyltriphenylphosphonium chloride or bromide DES following CNT oxidation and acidification, and the novel DES-functionalized CNT were applied as adsorbents of arsenic ions in water, revealing good maximum adsorption capacity. ChCl-based DES were used for the functionalization of CNT to be employed as adsorbents of lead ions from water [177]. Twenty-four different DES-CNT based adsorbents were prepared and characterized, exhibiting good adsorption capacities. Allyltriphenylphosphonium bromide/glycerol DES was chosen as the functionalization agent of CNT for the removal of mercury from water [178]. The novel adsorbents also revealed good maximum adsorption capacity. Recently, Abo-Hamad et al. [179] functionalized CNT using a variety of ammonium- and phosphonium-based DES. Evidence was provided for substantial chemical, structural and morphological changes in the CNT after functionalization with the DES, besides significant improvement of dispersion stability, surface areas and micropore volumes.

5. Conclusions

DES currently constitute an essential tool in the preparation of innovative and sophisticated materials, and have been making a significant contribution towards the development of new sustainable, efficient, economic and environmentally friendly processes. The present review highlights the advantages, relevance and potentialities of DES in the creation of novel materials with well-defined and appropriate characteristics, by safe and efficient procedures. Besides the three main fields focused on – polymer, metal processing and nanomaterials science – the replacement of conventional solvents and IL by these unique mixtures in other areas is definitely expected to become an increasingly common practice. A large amount of future research is thus anticipated and new breakthroughs will certainly be achieved in the near future.

Acknowledgments

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