Chapter 4
Applications of Deep Eutectic Solvents

Since their advent in 2003, deep eutectic solvents have found applications in numerous fields where their properties as solvents, permitting the dissolution of a large variety of solutes, and their being "green", i.e., ecologically friendly as described in Chap. 1, gave them advantages over more conventional solvents. It is possible in the present chapter to present only examples of the numerous applications that have been proposed over less than a score of years that have passed since the first publication regarding the deep eutectic solvents. Deep eutectic solvents (among other neoteric ones) have recently been reviewed for their use as green and sustainable solvents in chemical processes [1].

An application that cannot be classified under the headings of the following sections nor under those in Chap. 5 is the preparation of solid composite electrolytes for lithium/lithium-ion batteries. The deep eutectic solvent comprises 1:4 lithium bis(trifluorometanesulfonyl)imide as the hydrogen bond acceptor and *N*-methylacetamide as the hydrogen bond donor. This liquid was mixed with 1:8.7 tetraethoxysilane and formic acid in a sol–gel process, to form the so-called eutectogel as the battery electrolyte that is thermally stable to 130 °C and electrochemically stable up to 4.8 V [2].

4.1 Applications as Reaction Media

The use of deep eutectic solvents as reaction media is predicated on their being able to dissolve the reactants and any catalyst that is to be used, on their not being consumed in the reaction, on the ability to recover the product(s) of the reaction, and on the ability to recycle the solvent and catalyst, if used. With these conditions in mind, deep eutectic solvents have been chosen due to their being inexpensive, readily produced, and readily (bio)degradable, i.e., being "green". When

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commercially available DESs have been used as reaction media, they are noted in the following by their commercial names, as referred to in Chap. 2: Reline, Ethaline, Glyceline, and Maline.

Several reports for the use of deep eutectic solvents in the synthesis of inorganic materials have been published, many of them under the heading of "ionothermal synthesis". Metal oxides are soluble in DES based on choline chloride: Reline, Ethaline, and Maline [3]. The latter shows the largest solubility of metal oxides, being >0.5 mass% at 50 °C for V_2O_5, CrO_3, MnO, Mn_2O_3, FeO, and Co_3O_4, and >1.4 mass% for Cu_2O, CuO, and ZnO. Appreciable but lower solubilities are manifested in Maline by CoO, Fe_3O_4, V_2O_3, Fe_2O_3, and NiO. In Reline appreciable solubilities have V_2O_3, CrO_3, and ZnO, whereas in Ethaline the solubilities of metal oxides are generally small, except for Cu_2O and ZnO. The solutions have the metal ions complexed with chloride anions and may be used for the preparation of other complexes and compounds based on the metal ions. In a previous paper [4], solubilities at 50 °C of CuO, Fe_3O_4, and ZnO in Maline, and in choline chloride 1:1 with oxalic acid and 1:2 with phenylpropanoic acid were reported. When $CuCl_2 \cdot 2H_2O$ is dissolved in a series of DES (at 0.02 mol dm^{-3}), it forms transparent colored solutions ranging from yellow (in Ethaline) through yellowish-green (in Reline), blue (in Ethaline with added NH_3) to purplish blue (in Ethaline with added ethylenediamine) [5]. Lead oxide is added to the 3d elements dealt with above, and the solubilities of ZnO, Cu_2O, and PbO_2 in Reline at 60 °C, which are considerably larger than those of other metal oxides present in electric arc furnace dust, are described [6, 7] and this DES may be used for their processing.

Ionothermal synthesis of various inorganic materials in deep eutectic solvents that are liquid at room temperature has often been reported. A feature of the ionothermal synthesis is the structure directing ability of the eutectic solvent mixture, besides acting as the solvent. A list of such applications is presented in Table 4.1.

Eutectic mixtures based on choline chloride with various urea derivatives (1,3-dimethylurea, 2-imidazolone (1,2-ethyleneurea), and tetrahydro-2-pyrimidinone (1,3-propyleneurea)) have been employed for the production of aluminum phosphates [8], the urea derivative decomposed during the reaction and provided the template for the desired structure of the product. A layered gallium phosphate was prepared in an eutectic mixture consisting of choline chloride and imidazolidone [9] or tetrahydro-2-pyrimidinone [10] as a solvent and as a structure directing agent. Cobalt aluminophosphates were prepared by ionothermal synthesis in eutectic mixtures of choline chloride with succinic and glutaric acids (at 1:1 ratios) and with citric acid (at a 1:2 ratio) [11].

Novel vanadium fluorides and oxyfluorides were synthesized in a deep eutectic solvent based on choline chloride and 1,3-dimethylurea or 2-imidazolone (1,2-ethyleneurea) in the presence of hydrogen fluoride [12]. However, these template producing solvents are not proper deep eutectic solvents as defined in this book, since they are not liquid at room temperature and because a component of the solvent, the urea derivative, is consumed in the structure directing reaction. Only the eutectic formed from tetramethylammonium bromide and 1,3-dimethylurea,

Table 4.1 Ionothermal synthesis of inorganic materials in deep eutectic solvents

Deep eutectic solvent	Product	Ref.
Reline	MPO_4 (M = Mn, Fe, Co)	[295]
	Nanostructured nickel compounds	[296]
	Aluminum phosphate	[218]
	Cu(I) in chloride media	[297]
	Surface-modified silica particles	[298]
	Fe_2O_3 (haematite) nanospindles	[216]
	Fe_3O_4 magnetic nanoparticles	[299]
	Mg–A; layered double oxides	[300]
	$CoFe_2O_4@B_2O_3–SiO_2$	[28]
Ethaline	Nickel phosphide nanoparticles	[301]
	Nickel phosphide coatings	[302]
	Nickel oxide nanostructured films	[218]
Maline	Iron(III) hexacyanoferrate nanospheres	[251]
Choline chloride/oxalic acid	Oxalate-bridged lanthanide(III) chains	[303]
	Oxalate-bridged gadolinium polymers	[304]
Choline chloride/diethylene glycol	Zinc oxide nanoparticles	[224]
Choline chloride/pyrazole	Tin(II) phosphite alone and Mn-doped	[305]
Choline chloride/imidazolidone	Gallium phosphate, layered	[9]
Ethylammonium chloride/oxalic acid	Zirconium phosphate open framework	[306]
Me_4NCl/urea	Zirconium fluorophosphates	[307]
Me_4NCl/1,6-hexanediol	Sodalite, zeolite ZSM-39	[308]
Et_4NCl/pentaerythritol	Silicalite-1	[308]
Pr_4NBr/pentaerythritol	Silicalite-1, zeolite ZSM-5	[308]
Pr_4NBr/oxalic acid	Layered α-$Zr(HPO_4)_2 \cdot H_2O$	[306, 309]

among those tested in the study [8], has a melting point $\leq$25 °C and is a proper deep eutectic solvent.

There is an extensive list of reports dealing with the production of organic compounds in deep eutectic solvents, a subject that has also been reviewed in several publications [13–23]. These all stress the "green" aspect of the deep eutectic solvents: environmental friendliness, sustainability, biodegradability, as well as their direct utility in metal-catalyzed or non-catalyzed organic reactions. Biocatalysis by means of enzymes was another feature that was pointed out in these reviews [14, 16] and elsewhere [24–26].

The reactions that were reported as using deep eutectic solvents were Lewis acid-catalyzed dehydration of carbohydrates, hydrogenation of olefins, isomerization, cycloaddition to terminal azides and alkynes, and cross-coupling [16] as well as replacement, condensation and oxidation, and reduction reactions [18]. The synthesis of heterocyclic compounds as well as esterification and halogenation reactions in deep eutectic solvents featured in [23]. The hydrogen bond accepting (HBA) components of the deep eutectic solvents dealt with in these reviews

included choline chloride, ethylammonium chloride, and betaine (trimethylglycine) hydrochloride and the commonly used hydrogen bond donating (HBD) components included urea, ethylene glycol, glycerol, oxalic acid, malonic acid, and lactic acid [17], but many other HBA and HBD agents have also been used in deep eutectic solvents for organic reactions.

Reline is featured in a majority of the detailed reports on the use of deep eutectic solvent that are summarized in Table 4.2, which are but a sampling of the existing relevant publications. Some special features in the use of deep eutectic solvents as reaction media for organic synthesis is the use of ultrasound [27, 28], highly acidic

Table 4.2 Examples of organic reactions in deep eutectic solvents

Deep eutectic solvent	Reaction/product	Ref.
Reline	Bromination of a substituted quinone	[310]
	N-arylphthalimide derivatives	[311]
	Amino acid dithiocarbamates	[312]
	Peptide synthesis, chymotrypsin-catalyzed	[39]
	Oxazole synthesis, ultrasound-assisted	[27]
	Tricyanovinylated aromatics	[40]
	Redox isomerization of allyl alcohols to carbonyls	[31]
	Imine and hydrobenzamide synthesis	[313]
	Butyl acetate, lipase-catalyzed	[41]
	Disubstituted isoxazoles and isoxazolines	[314]
	Substituted pyridines	[315]
	Stereoselective reactions	[35]
	Aminoimidazoles	[316]
	Stereoselective organocatalyzed reactions	[36]
	Enantioselective aldol reaction	[37]
	Regio- and stereoselective synthesis	[38]
	Peroxidation reactions	[42]
	Benzofused seven-membered heterocycles	[317]
	Dihydroquinazolinones, catalytic synthesis	[28]
	Crude heavy oil hydrogenation with MoO_3	[56]

(continued)

Table 4.2 (continued)

Deep eutectic solvent	Reaction/product	Ref.
Ethaline	Butyl acetate, lipase-catalyzed	[41]
	Peroxidation reactions	[42]
Glyceline	Butyl valerate, lipase-catalyzed	[13]
	N-arylphthalimide derivatives	[311]
	Biocatalyzed reactions, transesterification	[14]
	Peptide synthesis, chymotrypsin-catalyzed	[39]
	Redox isomerization of allyl alcohols to carbonyls	[40]
	Butyl acetate, lipase-catalyzed	[41]
	Stereoselective reactions	[35]
	Aminoimidazoles	[316]
	Stereoselective organocatalyzed reactions	[36]
	Enantioselective aldol reaction	[37]
	Peroxidation reactions	[42]
	Cycloisomerization of a terminal alkyne	[31]
Maline	*N*-arylphthalimide derivatives	[311]
	Butyl valerate, lipase-catalyzed	[13]
Choline chloride 1:1 fructose	Stereoselective reactions	[35]
	Stereoselective organocatalyzed reactions	[36]
Choline chloride 1:2 lactic acid	Redox isomerization of allyl alcohols to carbonyls	[31]
Choline chloride + levulinic, + oxalic, or + *p*-toluenesulfonic acids	Cellulose nanocrystal production	[30]
Choline chloride + xylitol or + isosorbide	Peptide synthesis, chymotrypsin-catalyzed	[39]
Ethylammonium chloride + acetamide	Butyl valerate, lipase-catalyzed	[13]
+ urea, + ethylene glycol, + glycerol	Peroxidation reactions, biocatalyzed	[42]
Betaine hydrochloride + glycerol	Biocatalyzed reactions, transesterification	[14]
Betaine monohydrate + glycerol	Interaction with palmitic acid	[15]
Benzyltrimethylammonium methylsulfonate + *p*-toluene sulfonic acid	Esterification of carboxylic acids with alcohols	[30]

media [29, 30], metal catalysis [16, 17, 19, 31–34], stereo- or enantioselectivity [35–38], and biocatalysis [20, 24, 39–43].

Catalysis by the deep eutectic solvents themselves or as enzyme-friendly media has been stressed in some further publications, where, for instance, *Candida*

antarctica lipase A (CALA) and *Escherichia coli* TG1/pPBG11 are active in deep eutectic solvents [25, 44]. The activity, stability, and structure of the enzyme lactase from *Bacillus* HR03 in betaine-based natural deep eutectic solvents were studied in [26].

The eutectic solvent prepared from 1:2 choline chloride with zinc chloride is the solvent as well as the catalyst for transesterification reactions for biodiesel production [45]. It was also effective for the cycloaddition reaction of organic nitriles with sodium azide [46] and for acylation of secondary alcohols, phenols, and naphthols [47]. Deep eutectic solvents consisting of choline chloride with urea, glycerol, or *p*-toluene sulfonic acid act as both solvents and catalysts [48]. Deep eutectic solvents consisting of benzyltrimethylammonium chloride with *p*-toluene sulfonic acid, citric acid, or oxalic acid act as both solvent and catalyst in the esterification of acetic acid with butanol [49] or with 2-ethylhexanol [50]. Selective alkylation of imines and quinolines with organolithium reagents could be carried out fast at room temperature and in the presence of air in Glyceline solvent [51].

Deep eutectic solvents are also used for the preparation of heterogeneous catalysts used in catalytic reactions. Metallic gold with a large surface area is featured in several publications. Gold nanowire networks were prepared in Reline and in Ethaline, and were used in the catalytic reduction of 4-nitroaniline [52]. Monodisperse gold microparticles were prepared in Maline and used in the reduction of 4-nitrophenol [53]. Gold nanoparticles on a titania support were prepared in Reline and used in the selective hydrogenation of butadiene as catalysts [54]. Gold nanofoams were prepared in Ethaline and used in the reduction of aromatic nitro-compounds [55]. Molybdenum oxide catalyst for the upgrading of heavy crude oil was dissolved in Reline [56]. Reline was used for the preparation of nickel and nickel nitride nanoparticles used in catalytic reactions [57]. A sulfonic acid functionalized nanocatalyst based on a magnetic Fe_3O_4 on silica and titania surfaces was prepared in Reline [58]. A palladium catalyst with a pyridinophosphine ligand, usable in cross-coupling reactions, was successfully prepared in Reline [59]. A cross-dehydrogenative coupling reaction using copper oxide impregnated on magnetite as catalyst was carried out in Ethaline [60].

In those cases in which either the hydrogen bond accepting (HBA) or the hydrogen bond donating (HBD) component of the deep eutectic solvent is a monomer capable of polymerization, functional polymeric materials can result from free-radical polymerization, in this kind of solvent as well as of the solvent itself. An example of the monomeric HBA is choline methacrylate bromide at 2:1 with malonic acid and an example of the monomeric HBD is acrylamide at 1:2 with choline chloride forming the solvent [61]. Choline chloride was polymerized with methacrylic acid (1:2) while incorporating magnetite in order to produce a magnetic molecularly imprinted polymer for the selective recognition and separation of bovine hemoglobin [62]. Deep eutectic solvents were also used as reaction media for the production of molecularly imprinted polymers of which the solvent was not a monomer [63].

4.2 Biomass and Biodiesel Processes

Biomass from vegetation consists mainly of cellulose, with hemicellulose and lignin being minor components. The processes that are involved aim at decomposition of the biomass to sugars on the one hand and at esterification of the polysaccharides to useful products, such as cellulose acetate films or to fuels. For this purpose, the cellulose, hemicellulose, and lignin have to be solubilized in suitable solvents, and deep eutectic solvents have been suggested as neoteric "green" solvents for this purpose. The use of deep eutectic solvents for the fractionation of lignocellulosic biomass was reviewed in [61, 64] and along with ionic liquids in [65].

Molten salt hydrates have since many years been studied for their dissolving abilities of cellulose. Although these melts by themselves are not the eutectics dealt with in Chaps. 2 and 3, they readily are turned to the eutectics on dilution with the appropriate amount of water. This may have as a consequence the gelation of the dissolved cellulose, or its remaining in solution, depending on the salt, the temperature, and the concentration. The presence of small strongly hydrated cations (Li^+, Ca^{2+}, Zn^{2+}) and highly polarizable anions (I^-, SCN^-, ClO_4^-) is conducive to the dissolution of cellulose from biomass.

Zinc chloride hydrates featured in several of the investigations of cellulose dissolution. The tetrahydrate, $ZnCl_2{\cdot}4H_2O$, is liquid at room temperature and is highly acidic (more than neat phosphoric acid) [66]. It forms a eutectic with water at a mole ratio of 2.17 water per unit $ZnCl_2{\cdot}4H_2O$ with a melting point of −62 °C [67], but its use for the preparation of cellulose aerogels did not specify the composition of the salt hydrate solvent nor the temperature at which the dissolution of the cellulose was effected [68, 69]. The tetrahydrate was said to be able to swell cellulose but without forming a clear solution [70]. Other reports on the use of aqueous zinc chloride for the dissolution of cellulose did not specify a definite hydrate, but just salt hydrate melts. Dissolution of cellulose in aqueous 70 mass% zinc chloride has been described [71]. Conversion of cellulose to isosorbide mentioned molten hydrated zinc chloride (at mole fractions of $ZnCl_2 \geq 0.66$) as a solvent that solubilized cellulose due to interactions between the ionic species and hydroxyls, breaking the hydrogen-bonded network of the cellulose [72]. The presence of vicinal hydroxyl groups on the glucopyranoside rings of the cellulose was essential for the formation of the zinc chloride complex [70, 73]. The solubility of cellobiose increased with the aqueous zinc chloride concentration, this salt being more efficient than LiCl [74]. Cellulose dissolved to a clear solution in 68 mass% aqueous zinc chloride, from which solution cellulose-based films were readily prepared [75]. Aqueous zinc chloride, at concentrations above 29.6 mass%, effectively dissolves starch, another manifestation of a polysaccharide biomass [76].

Aqueous calcium thiocyanate is another medium commonly used for the dissolution of cellulose, although no information could be found on eventual eutectic formation from the salt hydrates with water. A solution boiling between 135 and 150 °C dissolves bleached cotton or wood pulp when heated to 80–100 °C, the

fiber gradually passing into a colloidal solution, but solutions boiling above or below these limits are not solvents for cellulose [77]. A 59 mass% solution dissolved cellulose at 120 °C, the solution turning to a porous gel on cooling [78]. A solution of calcium thiocyanate in water at 59 mass%, a composition corresponding to the hexahydrate, produced aerogels on the dissolution of the cellulose [69]. A lower concentration, $\geq$48.5 mass%, corresponding to the tetra- (or lower) hydrate was able to dissolve cellulose [79] and changes in the structure of wood pulp take place at 55 mass% concentration of this salt [80], whereas NaSCN at 60 mass% was rather ineffective for the dissolution [81].

Aqueous lithium salts are other media used for the dissolution and processing of cellulose. Molten lithium perchlorate trihydrate and iodide dihydrate, which do form deep eutectic solvents (see Chap. 2), yield transparent but viscous solutions of cellulose [82, 83]. In addition to these lithium salts, also the molten thiocyanate dihydrate dissolves cellulose [84]. Molten lithium acetate, chloride, and nitrate are not effective for the dissolution, although they do cause swelling of the cellulose [72, 84, 85]. On the contrary, molten lithium bromide hydrate, or the aqueous solution at 54–60 mass%, is quite effective for this purpose [86, 87].

Dissolution of cellulose in hydroxide media is possible but less effective than the aqueous salt media mentioned above. Dissolution in 8.5 mass% aqueous sodium hydroxide required hydrothermal and ethanol–acid pretreatments [88] and when applied to rice husks aqueous alkalis are able to dissolve the lignin (and the silica) but not the cellulose, whereas the latter can be dissolved in aqueous tetrapropyl- and tetrabutylammonium hydroxide [89].

No dissolution but in some cases fine dispersion and swelling was observed in several molten salt hydrates, including $LiCH_3CO_2{\cdot}2H_2O$, $LiNO_3{\cdot}3H_2O$, $Na_2S{\cdot}H_2O$, $NaCH_3CO_2{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}18H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$. The dissolution of cellulose in molten salt hydrates, summarized in Table 4.3, was reviewed in [90, 91], where the solvents were also used as reaction media for carboxymethylation and for acetylation of the dissolved cellulose.

Conventional deep eutectic solvents have also been tested as pretreatment agents of cellulose for various processes. Glyceline pretreatment was more effective than the use of Reline or the choline acetate/glycerol eutectic for subsequent enzymatic hydrolysis [91]. Reline was used, however, for studying the dissolution of cellulose fibers or their chemical derivatization [92]. Hydrothermal pretreatment of date palm residues served for the reduction of the recalcitrance of this biomass for dissolution in Glyceline and subsequent enzymatic digestion [93]. Microwave assistance was useful for the fractionation of lignocellulose in choline chloride/lactic acid deep eutectic solvent [94]. Lignin could be solubilized in a deep eutectic solvent consisting of betaine/lactic acid and be subsequently transformed into uniform nanoparticles [95]. Lignocellulosic biomass processing was tested with some deep eutectic solvents, such as those using betaine or choline chloride as the hydrogen bond accepting components and lactic, malic, oxalic, and other acids as the hydrogen bond donating components [96–98]. Of these, only the 1:2 betaine/lactic acid and 1:10 choline chloride/lactic acid were markedly effective, and only lignin but not starch nor cellulose were dissolved. In a two-stage process, using choline

Table 4.3 Processing of biomass in aqueous/molten salt hydrates

Salt	Process	Ref.
Zinc chloride	Cellulose aerogel preparation	[68, 69]
	Swelling of cellulose	[70]
	Dissolution of cellulose	[71]
	Conversion of cellulose to isosorbide	[72]
	Dissolution of cellobiose	[74]
	Dissolution and film production from cellulose	[75]
	Dissolution of starch from biomass	[76]
Calcium thiocyanate	Dissolution of cotton and wood pulp	[77]
	Dissolution of cellulose, porous gel formed on cooling	[78]
	Cellulose aerogel preparation	[69]
	Dissolution of cellulose	[79]
	Structure change of wood pulp	[80]
Lithium bromide	Dissolution of cellulose	[86, 87]
Lithium iodide	Dissolution of cellulose	[82, 83]
Lithium perchlorate	Dissolution of cellulose	[82, 83]
Lithium thiocyanate	Dissolution of cellulose	[84]
Sodium hydroxide	Dissolution of pretreated cellulose	[88]
	Dissolution of lignin	[89]
Pr_4NOH, Bu_4NOH	Dissolution of cellulose	[89]

chloride/oxalic acid in the first stage and Reline in the second, rice straw was effectively pretreated for enzymatic hydrolysis [99].

Biodiesel, referring to diesel fuel based on vegetable oil or animal fat, consists of methyl, ethyl, or propyl esters of long-chain alkyl carboxylic acids. It is typically made by chemically reacting lipids, such as vegetable oil, soybean oil, or animal fat (tallow), in a suitable solvent with an alcohol. A by-product of such reactions is glycerol that should be separated from the fuel, and deep eutectic solvents have been proposed for this task. The 1:1 mixtures of glycerol with choline chloride (i.e., not Glyceline, the 1:2 mixture), chloroethyltrimethylammonium chloride, and ethylammonium chloride were effective for the removal of the glycerol on biodiesel production from soybean and rapeseed oils [100]. Glyceline was tested for this purpose for biodiesel produced from palm oil [101]. More effective than Glyceline for this purpose were Ethaline and the choline chloride/trifluoroacetamide deep eutectic solvents [102] or those based on methyltriphenylphosphonium bromide with ethylene glycol or triethylene glycol [103]. Artificial neuron networks were employed in order to predict the efficiency of the removal of glycerol from the produced biodiesel and showed that phosphonium-based solvents were superior in this respect to ammonium-based ones [104]. Indeed, allyltriphenylphosphonium bromide/*p*-toluenesulfonic acid was the preferred medium for the esterification of oleic acid with glycerol to produce di- and triclycerides [105].

Another aspect of biodiesel production is the catalyst used for the esterification reaction. The same phosphonium solvent, namely, allyltriphenylphosphonium bromide/*p*-toluenesulfonic acid served well as a catalyst for the production of the methyl ester from crude palm oil [106]. Low-grade crude palm oil with a high fatty acid content could be effectively processed in diethylethanolammonium chloride/*p*-toluenesulfonic acid deep eutectic that acted both as solvent and as catalyst for the transesterification [107]. Whereas the glycerol-based deep eutectic solvents, Glyceline and methyltriphenylphosphonium bromide/glycerol, were not very effective for the elimination of glycerol from the biodiesel [101–103], they proved effective for the removal of the residual potassium hydroxide catalyst employed for the transesterification reaction [108].

Most of these reports dealt with biodiesel production from crude palm oil, but there are, of course, many other vegetable oil and animal fat sources for biodiesel fuel production. It ought to be mentioned that the waste glycerol from the biodiesel production is valuable as a component of deep eutectic solvents [109]. Rapeseed oil was treated in Glyceline as the solvent with a calcium oxide [110] or with sodium hydroxide catalyst [111] for the production of biodiesel. The oil from the Indian beech tree *Pongamia pinnata* was trans-esterified by methanol in the presence of sodium hydroxide catalyst in the 1:2 choline chloride/oxalic acid deep eutectic solvent [112]. Soybean oil was used for biodiesel preparation by transesterification with propanol or butanol, rather than the commonly used methanol, in choline chloride/glycerol and /ethylene glycol solvents at various compositions and with sodium alkoxide catalysis [113]. The 1:2 choline chloride/zinc chloride mixture is liquid at 25 °C and is an effective solvent for the preparation of biodiesel from soybean oil [114]. The high Lewis acidity of the mixture is conducive for the transesterification reaction. The influence of the type and purification of animal fat on the quality of the biodiesel produced from it in Ethaline was studied in [115].

Enzymatic catalysis was also applied to biodiesel production in deep eutectic solvents. *Millettia pinnata* seed oil was treated in a choline acetate/glycerol deep eutectic solvent with a suitable enzyme as the catalyst to produce biodiesel [116] the acetate eutectic being more effective than the commonly used chloride one. This was not the case for the enzymatic preparation of biodiesel from soybean oils, where the chloride eutectic was more efficient than the acetate one [117]. Both rapeseed oil and used acidic cooking oil were the sources for the enzymatic synthesis of biodiesel in Reline and Glyceline as solvents [118]. Yellow horn seed oil was the source for enzyme-catalyzed preparation of biodiesel in deep eutectic solvents, assisted by microwave irradiation, Glyceline proving to be the most efficient among the choline chloride-based solvents tested [119].

A microalgal biomass could be pretreated with aqueous choline chloride/oxalic acid (40 vol% water) or aqueous Ethaline (24 vol% water) to recover the lipid content for subsequent conversion to biodiesel [120]. The role of the water was to reduce the viscosity of the deep eutectic solvent. The same biomass was treated in a 1:3 choline chloride/acetic acid eutectic solvent to extract the lipid and convert it to diesel oil in a one-step process [121], this composition being more effective than those with formic, oxalic, and malonic acids.

Table 4.4 Biodiesel preparation in deep eutectic solvents

DES HBA	DES HBD	Ratio	Additional feature	Ref.
Choline Cl	Urea	1:2	Enzymatic catalysis	[118]
	Ethanediol	1:2	Glycerol removal	[99]
	Ethanediol	1:2	Addition of water	[120]
	Ethanediol	1:2	Na alkoxide catalysis	[113]
	Glycerol	1:1	Glycerol removal	[99]
	Glycerol	1:2	Glycerol removal	[101]
	Glycerol	1:2	CaO catalysis	[110]
	Glycerol	1:2	NaOH catalysis	[111]
	Glycerol	1:2	Na alkoxide catalysis	[113]
	Glycerol	1:2	Enzymatic catalysis	[117]
	Glycerol	1:2	Enzymatic catalysis	[118]
	Glycerol	1:2	Enzymatic catalysis, microwave asst.	[119]
	Acetic acid	1:3		[121]
	Oxalic acid	1:1		[120]
	CF_3CONH_2	1:2	Glycerol removal	[102]
	$ZnCl_2$	1:2	Lewis acidity catalysis	[114]
Choline acetate	Glycerol	1:2	Enzymatic catalysis	[116]
$EtNH_3Cl$	Glycerol	1:1		[99]
$Et_2EtOHNHCl$	pTSA[a]		*p*-toluene sulfonic acid catalysis	[118]
$ClEtMe_3N$ Cl	Glycerol	1:1	Glycerol removal	[99]
$MePh_3P$ Br	Ethanediol		Glycerol removal	[103]
	TEG[b]		Glycerol removal	[103]
$AllylPh_3P$ Br	pTSA[a]		*p*-toluene sulfonic acid catalysis	[106]

[a]*p*-toluene sulfonic acid
[b]triethylene glycol

The use of deep eutectic solvents for biodiesel production was reviewed in [122] and more recently in [123] and the results are summarized in Table 4.4.

4.3 Metal Electrodeposition and Electropolishing

From their earliest use as solvents, the deep eutectic fluids were found to dissolve metal oxides (see Sect. 4.1), and then the route to their use as electrolytes for metal electroplating was opened. Two deep eutectic solvents, now commercially available but readily prepared from their ingredients: Reline and Ethaline, have by far found the widest applications, as shown in Tables 4.5 and 4.6.

Electrochemical methods of investigation, cyclic voltammetry, and chronoamperometry have been extensively used for studying the electrodeposition of metals from deep eutectic solvents. The rate of nucleation is one aspect that has been studied, and its effect on the morphology of the deposited metals has been determined.

Table 4.5 Metals, metal alloys, and metal composites electrodeposition from Reline

Metal(s)	Additional features	Ref.
Ag	Mechanism of nucleation	[318]
	Thin film, nanoparticles	[129]
	Comparison with aqueous process	[124]
	Underpotential deposition	[130]
Au	Thin film, nanoparticles	[318]
	Shape-controlled nanocrystals	[131]
Au–Mn	Spectroscopic characterization	[319]
Co, Co–Sm	Magnetic deposits	[143]
Co–Pt	Magnetic film	[144]
Co–Sm	Magnetic film, nanowires	[132]
Cu	Also Al_2O_3, SiC composites	[152]
	Cu(I) stabilization in solution	[297, 320]
	Nanoporous film	[133]
	Dissolution of CuO	[321]
	Underpotential deposition	[322]
	Structural characterization	[164]
Cu–Ga	Precursor for $CuGaS_2$	[147, 148]
	Precursor for $Cu(InGa)S_2$	[149]
Cu–Ga–In	Precursor for $Cu(InGa)S_2$	[150, 323]
Cu–In	Precursor for $CuInSe_2$	[324]
Cu–Sn–Zn	Precursor for CZTS solar cells	[151]
Cu–Zn	Dissolution of CuO, ZnO	[325]
	Alloy film	[134]
Ga	Electrodeposition	[147]
In	Subsequent phosphoridation to InP	[326, 327]
Ni	Nanostructures	[135]
	Electrodeposition	[328]
	Electrodeposition	[173]
	Electrodeposition of nanostructures	[329]
Pb	Dissolution of PbO, submicrometer wires, powder	[330, 331]
	Dissolution of PbO, PbO_2, $PbSO_4$	[155]
	Nanoparticle aggregation	[332]
Pd	Nanoparticles	[136]
	Nanoparticles, thin film	[129]
	Shape control of deposited crystals	[333]
Pt	Nanoflowers for catalysis	[137]
	Nanocrystals	[138]
Sm	Electrodeposition	[143]
Sn	Electrodeposition	[163]
Zn	Metal nucleation	[334]

(continued)

Table 4.5 (continued)

Metal(s)	Additional features	Ref.
	Brightening by amine additives	[175]
	Composite with graphene oxide	[335]
	Deposition from dissolved arc furnace dust	[336]
Zn–Co	Electrodeposition	[337]
Zn–Mn	Boric acid additive	[338]
	Electrodeposition	[339]
	Electrodeposition	[340]
Zn–Ni	Electrodeposition	[341]
Zn–Sn	Effects of additives	[156]
Zn–Ti	Electrodeposition	[342]

Table 4.6 Metals, metal alloys, and metal composites electrodeposition from Ethaline

Metal(s)	Additional features	Ref.
Ag	Application of quartz microbalance	[343]
	Thin film, nanoparticles	[129]
	Underpotential deposition	[130]
	Composites with Al_2O_3 and SiC	[153]
	Iodine-assisted extracted from ores	[125]
	Nanoparticles on a glassy carbon support	[187]
Ag–Co	Magnetic multilayers	[145]
As	Electrodeposition	[344]
Au	Thin film, nanoparticles	[297]
	Iodine-assisted extracted from ores	[125]
	Au^+ speciation	[181]
Bi	From chlorometalate salts	[345]
Bi–Sn	From chlorometalate salts	[345]
	Effect of boric acid	[346]
Cd–Zn	Coatings	[347]
Co–Cr	Structure, corrosion resistance	[348]
Co–Fe	Magnetic films	[146]
Co–Fe–Ni	Films	[139]
Co–Ni	Concentration dependence	[349]
Co–Ni–Sn	Microstructure, use as cathode	[349]
Co–Sm	Films	[350]
Co–Sn	Microstructure, use as cathode	[351]
	Enhanced corrosion resistance	[352]
Cu	Composites with Al_2O_3 and SiC	[152]
	Dissolution of CuO	[321]

(continued)

Table 4.6 (continued)

Metal(s)	Additional features	Ref.
	Electrodeposition	[353]
	Galvanic replacement growth kinetics	[182]
	Superhydrophobic film	[354]
Cu–Sn	Electrodeposition	[355]
Cu–Zn	Iodine-assisted recovery from complex mixtures	[125]
Fe	Films, magnetic properties	[140]
	Concentration dependence	[356]
Ga–As	Iodine-assisted recovery from complex mixtures	[125]
In	Electrodeposition	[357]
Ni	Nanostructured films	[141]
	Concentration dependence	[349]
	Bright deposits, effect of additives	[176]
	Composite with SiO_2	[154]
	Comparison with aqueous bath	[358]
Ni–P	Coatings	[302]
Ni–Sn	Microstructure, use as cathode	[157]
Pb	Reduction of PbO to porous lead	[359]
	Reduction of PbO	[360]
	Reduction of PbO	[361]
	Recycling from perovskites	[362]
Pd	Thin film, nanoparticles	[129]
Sn	Effect of complexing agents	[157]
	Thin film, nanoparticles	[142]
	Application of quartz microbalance	[343]
	From chlorometalate salts	[345]
	Electrodeposition	[163]
Sn–Sb	Alloy powder	[363]
Zn	Brightening by amine additives	[175]
	Comparison with aqueous bath	[126]
	Effect of tartrate ions	[158]
	Mechanism of deposition	[364]
	Deposition of alumina support	[365]
	Effect of electrode potential	[366]
	Effect of amine additives	[159]
	Deposition of Ti/TiO_2	[367]
	Porous TiO_2 templates	[368]
Zn–Ni	Effect of additives	[160]
Zn–Sn	Speciation of zinc and tin ions	[369]
	Use for corrosion protection	[161]
	Effect of additives	[156]
Zn–Ni–Sn	Electrodeposition	[370]

Comparisons of the performance of deep eutectic solvents as the electrolytes with that of corresponding aqueous electrolytes have been made [124–127], and the advantages and drawbacks of each process have been discussed. The potential windows of deep eutectic solvents are wider (see Sect. 3.6.6) than those of aqueous electrolytes and the evolution of hydrogen at the cathode is absent in the former solvents. The effect of ultrasound on the electrodeposition of copper from Glyceline and from aqueous solutions, increasing the current densities, was studied [127], the differences being due to the different viscosities. The "green" nature of the deep eutectic solvents is an advantage [126], and the reduction in the amount of wastewater is another, but drag-out due to the higher viscosity of the deep eutectic solvent (in particular of Reline, but also of Ethaline) is a disadvantage. The rate of nucleation, both for anodic dissolution of silver and for cathodic deposition in Reline, is smaller than in aqueous solutions [124]. In the case of nickel electrodeposition, the viscosity and conductivity in Ethaline solvent were not the rate-limiting factors compared with aqueous solutions under the same conditions of temperature and concentration [125]. However, the speciation of the nickel in the two kinds of solvents is different, leading to different morphologies of the deposited metal: that in Ethaline being nanocrystalline, hence bright, compared with the microcrystalline morphology, hence matt appearance, of the deposit from aqueous solutions. Nickel was electrodeposited from an Ethaline solution on a stainless steel mesh with a controllable pore size for efficient oil/water separation [128].

In many cases, special morphologies of the deposited metals and alloys were the consequence of the choice of the deep eutectic solvents for the electrodeposition. Thin films consisting of nanoparticles or nanowires, or having nano-porosity have been the targeted deposits for many investigations [129–142]. Some such deposited metals are particularly effective as catalysts [131, 137]. Magnetic metal and alloy deposits have resulted in a number of studies of the use of deep eutectic solvents [132, 140, 143–146]. Precursors for photovoltaic compounds involving gallium and indium together with copper have been deposited from deep eutectic solvents [147–151], and composites involving alumina, silica, and silicon carbide were targeted in other studies [152–154]. Various additives to the deep eutectic solvent have been used to affect the deposited metal or alloy, and their effects have been studied [155–161].

Although Reline and Ethaline have been by far the most widely used deep eutectic solvents for the electrodeposition of metals and alloys, a few studies involved other solvents of this kind. Glyceline featured in the electrodeposition of cobalt [162] and of copper [127]. Choline chloride was also the hydrogen bond accepting component of the deep eutectic solvent formed with propylene glycol as the hydrogen bond donating agent for the electrodeposition of tin [163] and with oxalic and malonic acids for the electrodeposition of copper [164]. The deep eutectic solvent composed of 1:2 choline chloride/$CrCl_3 \cdot 6H_2O$ served well for the electrodeposition of thick, adherent, and crack-free films of chromium [165, 166]. Choline acetate was preferred over choline chloride as the component of the deep

eutectic solvent for the electrodeposition of α-brass (copper–zinc alloy) as a bright coating. The choline acetate contained 20 mass% of water and triethanolamine was added for obtaining the most suitable solvent [167]. Another chloride-free deep eutectic solvent that has been suggested is that based on choline dihydrogencitrate with ethylene glycol, used for the electrodeposition of copper [168].

Electropolishing of metal deposits is a process opposing the electrodeposition, in that it dissolves anodically oxide layers produced on metal coatings exposed to the atmosphere. The brightening of electrodeposited coatings can also be effected by the use of certain additives to the deep eutectic solvents that affect the dissolved metal species. Ethaline has been used effectively for the electropolishing of stainless steel [169–172] and the surface was characterized. Bright deposits of nickel [173] and a cobalt–platinum alloy [144] were obtained from Reline and of niobium [174] from Ethaline by electrochemical polishing. Ethylenediamine and ammonia were effective brightening agents for the electrodeposited zinc from Reline and from Ethaline [175]. Four additives: nicotinic acid, methylnicotinate, 5,5-dimethyl hydantoin, and boric acid were tested for obtaining bright nickel deposits from Ethaline [176]. The former two direct the crystal growth to the 111 orientation while the latter two direct it to the 220 orientation. The electrolytic removal of the iron-rich layer from nickel-based hot isostatic press consolidation was achieved in Ethaline [177].

A galvanic replacement reaction in Ethaline enabled the fabrication of nickel nanostructures on a copper-based template by reduction of $NiCl_4^{2-}$ [178]. Electro-less galvanic deposition of metallic silver on copper from Ethaline was studied in [179, 180], and the deposits were characterized using acoustic impedance spectroscopy, scanning electron (SEM), and atomic force (AFM) microscopies. Bright gold on nickel was produced by electro-less galvanic deposition from a solution of AuCN in Ethaline [181]. Galvanic replacement of copper was studied in [182].

The subject of electrodeposition of metals and alloys from deep eutectic solvents was reviewed early in the course of using deep eutectic solvents in [183, 184] and more recently in [185], where electropolishing was also dealt with. A caveat regarding the electrochemical decomposition of choline chloride-based deep eutectic solvents was published in [186]. Over longer periods of electrolysis in Ethaline several decomposition products were found, such as 2-methyl-1,3-dioxolane and chlorinated products, such as chloromethane and chloroform.

4.4 Applications in Nanotechnology

In this section are initially discussed non-electrochemical procedures for the preparation of nanostructured metals and alloys in deep eutectic solvents; the electrochemical procedures having been dealt with in the previous section [129–142, 187]. Subsequently are dealt with nonmetallic nanostructured substances prepared in deep eutectic solvents, such as metal oxides, other inorganic compounds, carbon nanotubes and graphene sheets, and nanofibers of organic polymers.

Silver nanoparticles, of narrow size distribution around 4.5 nm, were prepared and dispersed in Reline by laser ablation of a metallic silver plate [188]. Reports on other non-electrochemical nanostructured metals dealt with gold. Shape-controlled (star-shaped) gold nanoparticles were prepared in Reline by reduction of $HAuCl_4$ with ascorbic acid at room temperature [189]. A low energy sputter deposition of gold in Reline resulted in spherical gold nanoparticles of 5 nm diameter that tended to self-assemble at the surface of the liquid and in the bulk as well [190]. The self-assembly of the gold nanoparticles in Reline was also studied in [191, 192]. Gold microparticles with surface roughness of controlled monodisperse diameters of 1–5 μm were prepared in the Maline deep eutectic solvent by reduction of $HAuCl_4$ with ascorbic acid at 50 °C [53]. High-index facetted gold nanocrystals with enhanced electrocatalytic activities were produced in Reline [193]. Gold nanowire networks with average widths of 17 and 23 nm were prepared by reduction of $HAuCl_4$ with $NaBH_4$ in Reline and in Ethaline [52]. Gum Arabic was used to stabilize gold nanosheets [194] and nanoparticles [195], the deep eutectic solvent in the latter study consisting of 4:1:1 choline chloride, glycerol, and gallic acid (3,4,5-trihydroxybenzoic acid) and $HAuCl_4$ was the source of the gold. Gold nanofoams were produced in Ethaline by reduction of $HAuCl_4$ on a zinc foil [55]. Gold nanoparticles supported on functionalized nanosilica were produced in Reline for use as an electrochemical enzymatic glucose biosensor [196]. Titania-supported gold nanoparticles were prepared in 2:3 choline chloride/urea mixtures (not the 1:2 mixture, Reline) [54]. Gold–palladium core–shell nanoparticles were prepared on a graphite rod in a deep eutectic solvent [197]. Most of the applications of the gold nanoparticles described in this paragraph were in catalysis, although in one case, the gum Arabic stabilized nanoparticles, were used as an X-ray contrast agent [195].

Carbon nanotube-supported platinum–cobalt nanocrystallites were prepared in Ethaline, which showed enhanced methanol electrooxidation performance [198]. High-index facetted platinum concave nanocubes were grown on multi-walled carbon nanotubes in Reline [199]. Self-supported films consisting of nickel–molybdenum microspheres were produced electrochemically in Ethaline [200].

The preparation of inorganic oxide nanostructures in deep eutectic solvents has received an extensive amount of work. Mesoporous silica spheres, useful as packing materials in size-exclusion chromatography, were prepared in deep eutectic solvents consisting of Reline (with possible presence of arginine) [201] and in 1:1 ammonium fluoride as the hydrogen bond accepting component and ethylene glycol, 1,2-butanediol, or glycerol as the hydrogen bond donating one [202]. Self-organized titania "nanobamboos" were prepared in a deep eutectic solvent consisting of 1:1 choline chloride and succinic acid by anodic dissolution of titanium. The "nanobamboos" are nanotubes decorated with periodic exterior rings [203]. Titania nanosized powder was produced by anodization of titanium in Reline or in Ethaline in the presence of tetrabutylammonium bromide and ethanol [204]. The synthesis of nanostructured titania in deep eutectic solvents as well as in room temperature ionic liquids was recently reviewed in [205]. The synthesis of

nanoparticles of Mn_3O_4 was accomplished in an all-in-one system: Ethaline as solvent, reactant, and template [206]. A deep eutectic solvent resulted from choline chloride and tin(IV) chloride that was used for the preparation of tin/tin dioxide/carbon composites as electrodes for supercapacitors [207].

The preparation of magnetic nanoparticles based on iron oxides in deep eutectic solvents received a great deal of attention. Spherical magnetic Fe_3O_4 nanoparticles were prepared in Reline [208] and in Reline, Ethaline or 1:1 choline chloride/oxalic acid [209] by co-precipitation of hydrated iron(II) and iron(III) chlorides as solutes. A combined oxidative precipitation and ionothermal method was employed for the production of magnetic Fe_3O_4 nanoparticles in Reline or Ethaline [210]. Magnetic nanoparticles of Fe_3O_4 were coated by Reline using 3-iodopropyltrimethoxy-silane as a binder, for use as a catalyst [211]. Magnetic nanoparticles of Fe_3O_4 were also prepared in Ethaline [212] and Reline [213]. A core–shell nanoreactor consisting of Fe_3O_4@SiO_2 in Reline involving HSO_3^- sorbed on the silica and $NaNO_3$ was prepared ultrasonically assisted in [213]. A catalyst consisting of $CoFe_2O_4$@B_2O_3–SiO_2 as a hybrid magnetic composite nanostructure was prepared ultrasonically assisted in Reline [28]. Porous nanosheets, where much of the iron was replaced by cobalt to yield $Co_{2.7}Fe_{0.3}O_4$, were prepared in Reline by co-precipitation of hydrated cobalt(II) and iron(III) chlorides [214]. The iron in ferrite could also be replaced partly by M = Mg, Co, or Ni to produce MFe_2O_4 nanoparticles in 1:1 choline chloride/maleic acid deep eutectic solvent [215]. Haematite (Fe_2O_3) nanospindles were prepared in a one-step synthesis in Reline [216]. Microwave assistance was used in the preparation of Fe_2O_3 nanoparticles in Reline [217]. A prominent use of this magnetic nanostructure is as readily removed heterogeneous catalysts [180, 183–185]; other uses include that as readily recoverable adsorbents of Cu^{2+} [208] or Cd^{2+} and Pb^{2+} [209] or of organic wastes [214], or for storage of Li as a lithium electrode [216].

Other nanostructured metal oxides prepared in deep eutectic solvents include NiO as a film electrodeposited from a choline chloride-based electrolyte [218] or as nanocrystals of NiO with high-energy facets prepared in Reline [219] or mesoporous flower-like NiO electrodes prepared in Reline [220]. Nanostructures of ZnO, including twin cones and nanorods, were prepared by dissolution of ZnO in Reline and precipitation of it by an anti-solvent containing ethanol [221] and a similar procedure was used for the preparation of mesoporous ZnO nanosheets [222] and of Cu^{2+}-doped ZnO nanocrystals [223]. Ionothermal precipitation was used to obtain highly dispersive ZnO nanoparticles in Ethaline [224]. These ZnO-based materials showed good photocatalytic performance. Nanocrystalline SnO_2, of $\sim$4 nm grain size, used as anodes for lithium-ion batteries, was prepared from tin(II) chloride hydrate dissolved in deep eutectic solvents by precipitation with hydrazine hydrate [225]. An ionothermal method was used in choline chloride-based deep eutectic solvents to produce mesoporous SnO_2 structures involving two crystalline phases: orthorhombic and tetragonal [226]. Nanostructured ceria, CeO_2, was prepared in Reline that allowed morphology and porosity control [227].

Other nanostructured inorganic materials prepared in deep eutectic solvents belong mainly to two groups: binary sulfides and analogous materials and salts of

oxyacids. An exception is CuCl nanoparticles, prepared in Reline at room temperature by reduction of copper(II) chloride with ascorbic acid in the presence of polyvinylpyrrolidone [228]. Another exception is the ionothermal synthesis of nanoparticles of nickel phosphide with a core/shell structure in Ethaline [229]. The core is amorphous and is covered by shells of crystalline Ni_3P of various thickness. Such structures can be used for lithium storage in anodes of lithium batteries. Nanoparticles of BiOCl sensitized by Bi_2S_3 were prepared in a deep eutectic solvent and can be used as photocatalysts [230].

Self-supported porous Ni_3S_2 films were prepared in Ethaline on nanoporous copper [231], serving as electrocatalysts for hydrogen evolution reactions. The double sulfide $CuInS_2$ in the form of chalcopyrite-structured nanorods was prepared in Reline, assisted by microwave heating [232]. Nanoparticles of the triple sulfide Cu_2ZnSnS_4, known as CZTS used in photovoltaic devices, were prepared in Reline with thiourea as the sulfur source, acting as both solvent and template [233]. Porous $NiCo_2S_4$ was prepared by solvothermal synthesis in a deep eutectic solvent consisting of thiourea and polyethylene glycol (PEG 200) [234]. Mesoporous Ni–Mo sulfides supported on carbon were prepared in deep eutectic solvents consisting of choline chloride and glucose [235]. The self-assembly of nanoparticles of PbS to star-like microscale superstructures was studied in Reline as the deep eutectic solvent [236]. These films of PbS composed of highly oriented nano/microrods were prepared in Reline on a glass substrate by ionothermal synthesis [237]. A variety of binary metal sulfides is produced in a two-stage process in choline chloride/thioacetamide denoted as a deep eutectic solvent precursor (DESP). In the first stage, a metal salt is dissolved in the solvent at a low temperature and in the second stage, the metal–DESP complex is transformed to the binary metal sulfide by heating [238].

Various nano-particulate calcium phosphates, hydroxyapatites, and fluoroapatites were prepared in deep eutectic solvents. Monetite ($CaHPO_4$) nanoparticles were prepared in a one-step low-temperature reaction using an all-in-one (reactant, solvent, template) deep eutectic solvent consisting of 1:1 choline chloride/calcium chloride hexahydrate [239]. Amorphous calcium phosphate nanoparticles (with non-specified chemical formulae), evolving to calcium deficient hydroxyapatites (CDHA), were prepared in Reline and also in Ethaline and Glyceline [240–242]. The effects of reaction time, temperature, and natures of the precursors and the solvent were studied in these investigations. Mineral substituted hydroxyapatite was prepared in a choline chloride/thiourea deep eutectic solvent [243]. On the other hand, nanocrystalline hydroxyapatite powder was prepared in Reline [244] as was the analogous fluoroapatite [245]. Bioactive fluoroapatite nanoparticles were prepared in a choline chloride–calcium chloride medium [246]. Emphasis in these studies was placed also on the recovery of the deep eutectic solvent for reuse in the synthetic processes.

A few other nanoparticles of salts of oxyacids were prepared in deep eutectic solvents. These include spindle-like nanoparticles of lithium manganese phosphate, prepared ionothermally in Ethaline by microwave heating [247, 248]. Ferroelectric barium titanate nanoparticles were prepared in 1:1 choline chloride/malic acid [249]

and spindle-like nanotubes of bismuth vanadate were prepared in Reline [250] ionothermally. Non-oxyacid salt nanoparticles that were prepared in deep eutectic solvents include nanospheres with controlled sizes of Prussian blue, prepared in 1:1 choline chloride/malic acid by addition of $FeCl_3 \cdot 6H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$ to the deep eutectic solvent [251]. Nanostructured electropolymerized poly(methylene blue) films were prepared in Ethaline [252].

Carbon nanotubes (CNTs) are another kind of materials prepared in deep eutectic solvents, which may be single-walled or multi-walled or composites with other substances. Polycondensation of resorcinol with formaldehyde in Ethaline, containing a small amount of water introduced with the formaldehyde, yielded the desired multi-walled carbon tubes after heat treatment with ready recycling of the Ethaline solvent [253]. Single-walled and double-walled carbon nanotubes were prepared by polycondensation of furfuryl alcohol in the highly acidic 1:1 choline chloride/*p*-toluenesulfonic acid deep eutectic solvent [254]. A deep eutectic solvent comprising choline chloride and acrylic acid was used both as a solvent and as the reactant to form HNO_3-functionalized carbon nanotube composites with poly (acrylic acid) that were macroporous [255]. Multi-walled carbon nanotube composites with nickel were electrodeposited from Reline containing nickel chloride on a copper substrate [256]. Carbon nanotubes prepared separately were subsequently functionalized by treatment with $KMnO_4$ or with HNO_3 in two phosphonium-based deep eutectic solvents: 1:1 methyltriphenylphosphonium bromide/glycerol and 1:16 benzyltriphenylphosphonium chloride/glycerol [257]. The resulting material was used for the absorption of arsenic species from water. A different deep eutectic solvent, comprised of 1:1 tetrabutylammonium bromide/glycerol was used to functionalize carbon nanotubes with KMnO4 for producing a material efficiently removing mercury species from water [258]. Magnetic multi-walled carbon nanotubes (MMWCNTs) were dispersed in a deep eutectic solvent comprised of 1:2 choline chloride/resorcinol for microextraction purposes [259]. MMWCNTs were also covered with Reline to form magnetic bucky gels for similar purposes [260]. Reline was also used for the electrodeposition of nickel on carbon nanotubes [261]. Multi-walled carbon nanotubes were treated in Reline with nitric acid and then with $PdCl_2$ and $SnCl_2$ solutions in Reline to produce the PdSn alloy supported on the nanotubes by sonication to be used as catalysts [262]. Allyltriphenylphosphonium bromide/glycerol was the deep eutectic solvent used to functionalize carbon nanotubes for the removal of mercury from water [263]. Ethaline was used for the synthesis of carbon nanotubes functionalized with redox-active poly(methylene blue) [264].

Another form of nanostructured carbon is graphene, and this was produced in deep eutectic solvents too. The interface between graphene and deep eutectic solvents consisting of choline chloride with urea, glycerol, malonic, levulinic, or phenylacetic acids was elucidated in [265]. Various such solvents (Reline, Ethaline, Glyceline, 1:2 choline chloride/di- and triethylene glycol, Maline, and methyltriphenylphosphonium bromide/glycerol, among several others) were used to reduce graphene oxide, formed by oxidation with $KMnO_4$, to produce functionalized graphene with hydrophilic groups [266]. Magnetic graphene oxide

nanoparticles were prepared in Ethaline or Glyceline by incorporation of Fe_3O_4 treated with 3-aminopropyltriethoxysilane in the core/shell structures, which were used for the extraction of proteins [267]. Carboxamide functionalized graphene oxide complexed with copper nanoparticles as a catalyst was prepared in Glyceline [34]. Graphene oxide treated with choline chloride/NaH_2PO_4 as a deep eutectic solvent was a high potency flame retardant [268]. Magnetic graphene oxide nanoparticles coated with a deep eutectic solvent (Glyceline or choline chloride/phenol or /tetrahydro-tetramethylnaphthol-2) using ultrasound assistance was used for drug pre-concentration [269]. Fresh seaweed was converted to functionalized graphene nanosheets (doped with Fe_3O_4) in a deep eutectic solvent comprising choline chloride/$FeCl_3 \cdot 6H_2O$ [270], which could be used as electrocatalysts. Graphene sheets derived from seaweeds were treated with deep eutectic solvents, comprising choline chloride and a metal (iron(III), zinc, or tin(II)) chloride, and were used for the removal of fluoride from water [271]. Functionalized graphene oxide nanoparticles dispersed by ultrasonication in 1:3 choline chloride/triethylene glycol and in 1:4 and 1:5 methyltriphenylphosphonium bromide/ethylene glycol deep eutectic solvents were proposed as new heat transfer fluids with enhanced thermal conductivity [272].

Mesoporous silica (SBA-15) was used as a support for deep eutectic solvents to be used as catalysts. The solvent consisting of *N*-methylpyrrolidine hydrochloride/zinc chloride was thus immobilized on mesoporous silica in [273, 274]. Nanoflowers consisting of copper phosphate on which *C. antarctica* lipase B enzyme was immobilized were prepared in Reline and in ethylammonium chloride/ethylene glycol deep eutectic solvents [275].

Nanostructured polymeric materials were prepared advantageously in deep eutectic solvents both electrochemically and otherwise. Conducting polyaniline films were prepared electrochemically in 1:2 choline chloride/1,2-propanediol deep eutectic solvent [276]. The films were nano-particulate and could be doped/dedoped reversibly, exhibiting fast charge transport across the film. Several other choline-based mixtures: Reline, Ethaline, and Glyceline, could also be used for the electrochemical preparation of polyaniline [277] the morphology, stability, and electrochromism of the products having also been studied. These three deep eutectic solvents were used for the electrochemical deposition of the conducting poly(3,4-ethylenedioxythiophene) film on glassy carbon electrodes [278], that could be used for sensing ascorbic acid, dopamine, and uric acid. Elastin-like recombinamers were prepared in Reline from several pentapeptides [279], their conformation in the collapsed state being stable even in the presence of water. The preparation of porous molecularly imprinted polymers (MIP) in various deep eutectic solvents for analytical purposes was described in [201].

Natural materials were transformed into nanofibers in deep eutectic solvents, for example, wood cellulose [280] and paper and board cellulose [281] that were pretreated in Reline before undergoing nanofibrillation. Cellulose was converted to nanofibrils by treatment with deep eutectic solvents comprising either ammonium thiocyanate/urea or guanidinium chloride/urea [282]. Silylated cellulose nanofibrils that were hydrophobic and super-absorbing aerogels were prepared in Reline [283]. Agar was advantageously made electro-spinnable in Reline [284] compared with

aqueous media, producing elastic nanofibers. Unbleached mechanical wood pulp was converted to nanofibers by treatment with a deep eutectic solvent made from triethylammonium chloride and imidazole [285]. Chitin nanofibers were prepared in a 1:2 choline chloride/thiourea deep eutectic solvent but not in Reline [286]. Lysozyme from hen eggs was transformed into nanofibers in a deep eutectic solvent involving choline chloride and acetic acid [287]. Guanine-rich oligonucleotide quadruplexes have the potential to control the bottom-up synthesis of nanoarchitectures, and two such oligonucleotides were prepared in Reline [288]. Nanocrystalline cellulose could be prepared in deep eutectic solvents comprising choline chloride and oxalic, *p*-toluenesulfonic, or levulinic acids, by mechanical disintegration of the primarily produced nanofibers from wood cellulose [29]. Cellulose nanocrystals were also produced from cotton by treatment with choline chloride/oxalic acid dihydrate deep eutectic solvent [289]. The cellulose nanocrystals produced in choline chloride/oxalic acid dihydrate deep eutectic solvent could then be used to stabilize marine diesel oil-in-water emulsions [290].

Microemulsions in the "pre-ouzo" state were obtained in the absence of a surfactant and water in Reline and 1:4 choline chloride/ethylene glycol deep eutectic solvents [291]. These fluctuations in the nonhomogeneous liquid were not due to an amphiphilic effect. Deep eutectic solvents consisting of alkylammonium chloride or bromide (alkyl = ethyl, propyl, butyl, or pentyl) and ethylene glycol or glycerol are nanostructured, as shown by X-ray scattering, and consequently, phospholipids form bilayer phases or vesicles in them [292]. Bucky gels, consisting of Reline and magnetic multi-walled carbon nanotubes, were prepared by treating carbon nanotubes with nitric acid, then adding $FeCl_2$ and $FeCl_3$ and co-precipitating Fe_3O_4 with the nanotubes by addition of a base [260]. They could be used as dispersive solid extractants for the determination of trace organochlorine pesticides.

The field of nanotechnological applications of deep eutectic solvents was reviewed in [293] and [294]. These solvents can be used to prepare well-defined nanomaterials, shape-controlled nanoparticles, films, metal-organic frameworks, colloidal assemblies, hierarchically porous carbons, and DNA/RNA architectures. They act as supramolecular templates as well as reactants. The moderate to large viscosities of the deep eutectic solvents are conducive to the ability of nanoparticle dispersions to be formed, retaining the large surface area-to-volume ratios conducive to catalytic activity, rather than allowing rapid growth to macrocrystalline moieties. These modes of operation of deep eutectic solvents make them useful in nanotechnology, additional to their low costs, ready availability, and "green" nature.

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