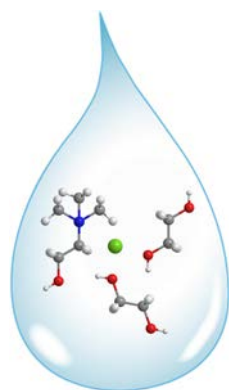


Deep Eutectic Solvents (DESs) and Their Applications

Emma L. Smith,^{*,†,‡} Andrew P. Abbott,[‡] and Karl S. Ryder[‡][†]Department of Chemistry, School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, United Kingdom[‡]Department of Chemistry, University of Leicester, Leicester LE1 7RH, United Kingdom

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1. INTRODUCTION

Deep eutectic solvents (DESs) are now widely acknowledged as a new class of ionic liquid (IL) analogues because they share many characteristics and properties with ILs. The terms DES and IL have been used interchangeably in the literature though it is necessary to point out that these are actually two different types of solvent. DESs are systems formed from a eutectic mixture of Lewis or Brønsted acids and bases which can contain a variety of anionic and/or cationic species; in contrast, ILs are formed from systems composed primarily of one type of discrete anion and cation. It is illustrated here that although the physical properties of DESs are similar to other ILs, their chemical properties suggest application areas which are significantly different.

The research into ionic liquids (ILs) has escalated in the last two decades, ever since the potential for new chemical technologies was realized. In the period covered by this review, approximately 6000 journal articles have been published on the topic. Compared to classical ILs, the research into DESs is comparatively in its infancy, with the first paper on the subject only published in 2001.¹ However, with publications from the past decade now approaching 200 an increasing amount of research effort is focusing on this emerging field. This is a comprehensive review encompassing all research areas and applications relating to DES publications between 2001 and the beginning of 2012. The chief focuses are the two major application areas of deep eutectic solvents (DESs): metal processing and synthesis media. A large proportion of research effort has been focused on the use of DESs as alternative media for metals that are traditionally difficult to plate or process, or involve environmentally hazardous processes. DESs have also been proposed as environmentally benign alternatives for synthesis.

1.1. Deep Eutectic Solvents

DESs contain large, nonsymmetric ions that have low lattice energy and hence low melting points. They are usually obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between for example a

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halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components.¹ In a 2001 study by Abbott et al. a range of quaternary ammonium salts were heated with ZnCl_2 and the freezing points of the resulting liquids measured. It was found that the lowest melting point, 23–25 °C, was obtained when choline chloride was used as the ammonium salt.¹ This initial study has been extended, and a range of liquids formed from eutectic mixtures of salts and hydrogen bond donors have now been developed.² These liquids were termed deep eutectic solvents to differentiate them from ionic liquids which contain only discrete anions. The term DES refers to liquids close to the eutectic composition of the mixtures, i.e., the molar ratio of the components which gives the lowest melting point (discussed in more detail in section 2).

Deep eutectic solvents can be described by the general formula



where Cat^+ is in principle any ammonium, phosphonium, or sulfonium cation, and X^- is a Lewis base, generally a halide anion. The complex anionic species are formed between X^- and either a Lewis or Brønsted acid Y (z refers to the number of Y molecules that interact with the anion). The majority of studies have focused on quaternary ammonium and imidazolium cations with particular emphasis being placed on more practical systems using choline chloride, $[\text{ChCl}, \text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3\text{Cl}^-]$.

DESs are largely classified depending on the nature of the complexing agent used, see Table 1. DESs formed from MCl_x

Table 1. General Formula for the Classification of DESs

type	general formula	terms
type I	$\text{Cat}^+\text{X}^-z\text{MCl}_x$	$\text{M} = \text{Zn},^{1,5,6} \text{Sn},^7 \text{Fe},^8 \text{Al},^8 \text{Ga},^9 \text{In}^{10}$
type II	$\text{Cat}^+\text{X}^-z\text{MCl}_x \cdot y\text{H}_2\text{O}$	$\text{M} = \text{Cr},^{11} \text{Co}, \text{Cu}, \text{Ni}, \text{Fe}$
type III	$\text{Cat}^+\text{X}^-z\text{RZ}$	$\text{Z} = \text{CONH}_2,^{12} \text{COOH},^{13} \text{OH}^{14}$
type IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}^-$	$\text{M} = \text{Al}, \text{Zn}$ and $\text{Z} = \text{CONH}_2, \text{OH}$

and quaternary ammonium salts, type I, can be considered to be of an analogous type to the well-studied metal halide/imidazolium salt systems. Examples of type I eutectics include the well-studied chloroaluminate/imidazolium salt melts and less common ionic liquids formed with imidazolium salts and various metal halides including FeCl_2 ,³ and those featured in Scheffler and Thomson's study with EMIC and the following metal halides: AgCl , CuCl , LiCl , CdCl_2 , CuCl_2 , SnCl_2 , ZnCl_2 , LaCl_3 , YCl_3 , and SnCl_4 .⁴

The range of nonhydrated metal halides which have a suitably low melting point to form type I DESs is limited; however, the scope of deep eutectic solvents can be increased by using hydrated metal halides and choline chloride (type II DESs). The relatively low cost of many hydrated metal salts coupled with their inherent air/moisture insensitivity makes their use in large scale industrial processes viable.

Type III eutectics, formed from choline chloride and hydrogen bond donors, have been of interest due to their ability to solvate a wide range of transition metal species, including chlorides¹⁵ and oxides.^{15,16} A range of hydrogen bond donors have been studied to date, with deep eutectic solvents formed using amides, carboxylic acids, and alcohols (see Figure 1). These liquids are simple to prepare, and relatively unreactive with water; many are biodegradable and are relatively low cost. The wide range of

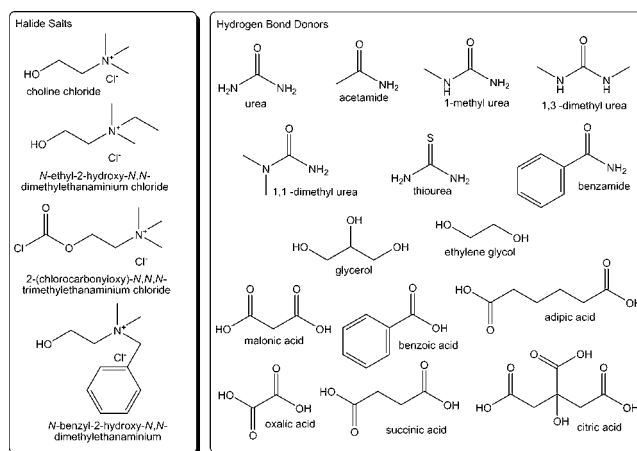


Figure 1. Structures of some halide salts and hydrogen bond donors used in the formation of deep eutectic solvents.

hydrogen bond donors available means that this class of deep eutectic solvents is particularly adaptable. The physical properties of the liquid are dependent upon the hydrogen bond donor and can be easily tailored for specific applications. Although the electrochemical windows are significantly smaller than those for some of the imidazolium salt–discrete anion ionic liquids, they are sufficiently wide to allow the deposition of metals such as Zn with high current efficiencies. This class of deep eutectic solvents have been shown to be particularly versatile, with a wide range of possible applications investigated including the removal of glycerol from biodiesel,¹⁷ processing of metal oxides,¹⁶ and the synthesis of cellulose derivatives.¹⁸

A majority of ionic liquids which are fluid at ambient temperatures are formed using an organic cation, generally based around ammonium, phosphonium, and sulfonium moieties. Inorganic cations generally do not form low melting point eutectics due to their high charge density; however, previous studies have shown that mixtures of metal halides with urea can form eutectics with melting points of <150 °C.^{19,20} Abbott et al. have built upon this work and shown that a range of transition metals can be incorporated into ambient temperature eutectics, and these have now been termed type IV DESs. It would be expected that these metal salts would not normally ionize in nonaqueous media; however, ZnCl_2 has been shown to form eutectics with urea, acetamide, ethylene glycol, and 1,6-hexanediol.²¹

Most of the deep eutectics reviewed here are based on the quaternary ammonium cation: choline [also known as the cholinium cation, (2-hydroxyethyl)-trimethylammonium cation and $\text{HOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$]. This cation is nontoxic and has a comparatively low cost (when compared with imidazolium and pyridinium). It is classified as a provitamin in Europe and is produced on the megatonne scale as an animal feed supplement. It is produced by a one step gas phase reaction between HCl , ethylene oxide, and trimethylamine and as such produces negligible ancillary waste.

1.2. Brief Description of Ionic Liquids

While this review is not concerned with conventional ionic liquids, it seems prudent, nevertheless, to discuss them in brief as some comparison must be made between DESs and ILs. Ionic liquids (ILs) have been one of the most widely studied areas in science in the past decade and are probably subject to more reviews per research paper than any other current topic.^{22–24}

The arbitrary definition that an ionic liquid is a class of fluid which consists of ions and are liquid at temperatures $<100\text{ }^{\circ}\text{C}$ was used traditionally to differentiate between ionic liquids and classical molten salts, which melt at higher temperatures; however, ionic liquids are now generally referred to as solvents which consist solely of ions. The traditional definition was first used to describe chloroaluminate based ionic fluids.²⁵ A major limitation of the chloroaluminate ionic liquids is their inherent air and moisture sensitivity, due to the rapid hydrolysis of AlCl_3 upon contact with moisture. The moisture sensitivity of these systems can be somewhat reduced by the replacement of AlCl_3 with more stable metal halides such as ZnCl_2 to form eutectic based ionic liquids.²⁶ The ionic liquids formed from organic cations with AlCl_3 and ZnCl_2 are often termed first generation ionic liquids.²² This class of ionic liquids are fluid at low temperatures due to the formation of bulky chloroaluminate or chlorozincate ions at eutectic compositions of the mixture. This reduces the charge density of the ions, which in turn reduces the lattice energy of the system leading to a reduction in the freezing point of the mixture.

The second generation of ionic liquids are those that are entirely composed of discrete ions, rather than the eutectic mixture of complex ions seen in the first generation ionic liquids. Wilkes and Zaworotko, working with alkylimidazolium salts, discovered that air and moisture stable liquids could be synthesized by replacing the AlCl_3 used in the eutectic ionic liquids with discrete anions such as the tetrafluoroborate and acetate moieties.²⁷ Although generally air and moisture stable, some studies have observed that exposure to moisture affects their chemical and physical properties, with the development of HF as water content increases.²⁸ The stability of this class of ionic liquids can be improved by using more hydrophobic anions such as trifluoromethanesulfonate (CF_3SO_3^-), bis-(trifluoromethanesulfonyl)imide [$(\text{CF}_3\text{SO}_2)_2\text{N}^-$], and tris-(trifluoromethanesulfonyl)methide [$(\text{CF}_3\text{SO}_2)_3\text{C}^-$].^{28–30} These systems have the additional benefit of large electrochemical windows, allowing less noble metals, inaccessible from the chloroaluminate liquids, to be electrodeposited.²⁸

In summary, the most widely used ionic liquids can be split into two distinct categories, those formed from eutectic mixtures of metal halides (such as AlCl_3) and organic salts (generally nitrogen based and predominantly with halide anions), and those containing discrete anions such as PF_6^- or bis-(trifluoromethanesulfonyl) imide. It is estimated that the total number of possible ionic liquids could be in the range of 10^6 distinct systems. Clearly ionic liquids have the potential to be highly versatile solvents, with properties which can be easily tuned for specific uses. However, if ionic liquids are to be successful as viable alternatives to aqueous electrolytes, they must also be simple and economic to synthesize.³¹

2. PROPERTIES OF DESs

While DESs and conventional ILs have different chemical properties, they have similar physical properties, in particular the potential as tunable solvents that can be customized to a particular type of chemistry; they also exhibit a low vapor pressure, relatively wide liquid-range, and nonflammability. DESs have several advantages over traditional ILs such as their ease of preparation, and easy availability from relatively inexpensive components (the components themselves are toxicologically well-characterized, so they can be easily shipped for large scale processing); they are, however, in general less chemically inert. The production of DESs involves the simple mixing of the two

components, generally with moderate heating. This maintains a comparatively low production cost with respect to conventional ILs (such as imidazolium based liquids) and permits large scale applications. While the individual components of DESs tend to be individually well toxicologically characterized, there is very little information about the toxicological properties of the eutectic solvents themselves, and this needs to be further investigated by the scientific community. The data from the few publications addressing this issue is presented in section 2.6. The term deep eutectic solvent was coined initially to describe type III eutectics but has subsequently been used to describe all of the eutectic mixtures described above. This is a logical approach, and although this includes all of the early work on haloaluminates, this is already the subject of numerous reviews and will not be dealt with here other than in comparative terms.^{32–34}

2.1. Phase Behavior

The difference in the freezing point at the eutectic composition of a binary mixture of A + B compared to that of a theoretical ideal mixture, ΔT_f , is related to the magnitude of the interaction between A and B. The larger the interaction; the larger will be ΔT_f . This is shown schematically in Figure 2. Considering first

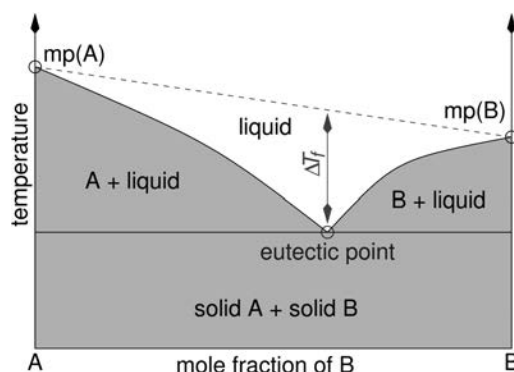


Figure 2. Schematic representation of a eutectic point on a two-component phase diagram.

the type I eutectics: the interactions between different metal halides and the halide anion from the quaternary ammonium salt will all produce similar halometallate species with similar enthalpies of formation. This suggests that ΔT_f values should be between 200 and 300 $^{\circ}\text{C}$. It has been observed that to produce a eutectic at about ambient temperature the metal halide generally needs to have a melting point of approximately 300 $^{\circ}\text{C}$ or less. It is evident therefore why metal halides such as AlCl_3 (mp = 193 $^{\circ}\text{C}$),³⁵ FeCl_3 (308),³⁶ SnCl_2 (247),³⁷ ZnCl_2 (290),³⁷ InCl_3 (586),³⁸ CuCl (423),³⁹ and GaCl_3 (78)⁴⁰ all produce ambient temperature eutectics. While unstudied to date, it could also be predicted that metal salts such as SbCl_3 (mp = 73 $^{\circ}\text{C}$), BeCl_2 (415), BiCl_3 (315), PbBr_2 (371), HgCl_2 (277), and TeCl_2 (208) should also form ambient temperature eutectics. The same is true of the quaternary ammonium salts where it is the less symmetrical cations which have a lower melting point and therefore lead to lower melting point eutectics. This explains why imidazolium halides C_2mimCl (mp = 87 $^{\circ}\text{C}$) and C_4mimCl (65 $^{\circ}\text{C}$) have superior phase behavior and mass transport to ChCl (301 $^{\circ}\text{C}$).

Type II eutectics were developed in an attempt to include other metals into the DES formulations. It was found that metal halide hydrates have lower melting points than the corresponding anhydrous salt. Clearly the waters of hydration decrease the

melting point of metal salts because they decrease the lattice energy. As Figure 2 shows, a lower melting point of the pure metal salt will produce a smaller depression of freezing point ΔT_f . This correlation can be seen in Figure 3 for the data presented in

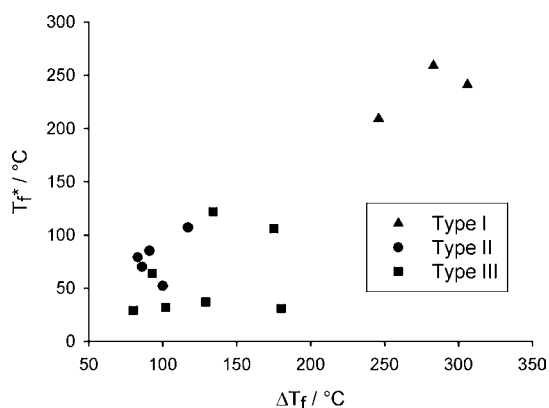


Figure 3. Correlation between the freezing temperature and the depression of freezing point for metal salts and amides when mixed with choline chloride in 2:1 ratio, where the individual points represent different mixtures.

the literature (Table 2)^{1,11,12,41} and arises because salts with a lower lattice energy will tend to have smaller interactions with the chloride anion. The only system fully described to date is that of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$,¹¹ although others including $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are

described in the patent literature.² Most of the systems studied have had phase diagrams similar to that shown in Figure 2; a small number of systems containing AlCl_3 , FeCl_3 , and SnCl_2 have each shown two eutectic points when mixed with imidazolium chlorides at approximately 33% and 66% metal halide. The type III eutectic mixtures depend upon the formation of hydrogen bonds between the halide anion of the salt and the HBD; where these HBDs are multifunctional, the eutectic point tends to be toward a 1:1 molar ratio of salt and HBD.¹³ In the same study the depression of freezing point was shown to be related to the mass fraction of HBD in the mixture.

2.2. Density, Viscosity, Conductivity, and Surface Tension

Mjalli et al. proposed a method for predicting the density for DESs at different temperatures.⁴³ The values of measured and predicted densities were compared, and the average of absolute relative percentage error (ARPE) for all the DESs tested was found to be 1.9%. The effect of salt to HBD molar ratio on ARPE in predicted DES densities was also investigated. The same group has also studied DESs formed from phosphonium based salts with different hydrogen bond donors.⁴⁴ Melting temperature, density, viscosity, pH, conductivity, and dissolved oxygen content were measured as a function of temperature. The authors found that the type of salt and HBD and the mole ratio of both compounds had a significant effect on the studied properties.

Table 3 shows selected typical physical properties for a variety of DESs at the eutectic composition at 298 K and compares this with ionic liquids with discrete anions and some molecular solvents. DESs are quite high in terms of their viscosity and lower

Table 2. Freezing Point Temperatures of a Selection of DESs

halide salt	mp/°C	hydrogen bond donor (HBD)	mp/°C	salt:HBD (molar ratio)	DES T_f /°C	ref
ChCl	303	urea	134	1:2	12	13
ChCl	303	thiourea	175	1:2	69	12
ChCl	303	1-methyl urea	93	1:2	29	12
ChCl	303	1,3-dimethyl urea	102	1:2	70	12
ChCl	303	1,1-dimethyl urea	180	1:2	149	12
ChCl	303	acetamide	80	1:2	51	12
ChCl	303	banzamide	129	1:2	92	12
ChCl	303	ethylene glycol	-12.9	1:2		
ChCl	303	glycerol	17.8			
ChCl	303	adipic acid	153	1:1	85	13
ChCl	303	benzoic acid	122	1:1	95	13
ChCl	303	citric acid	149	1:1	69	13
ChCl	303	malonic acid	134	1:1	10	13
ChCl	303	oxalic acid	190	1:1	34	13
ChCl	303	phenylacetic acid	77	1:1	25	13
ChCl	303	phenylpropionic acid	48	1:1	20	13
ChCl	303	succinic acid	185	1:1	71	13
ChCl	303	tricarballic acid	159	1:1	90	13
ChCl	303	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	116	1:1	16	42
methyltriphenylphosphonium bromide	231–233	glycerol	17.8		-4.03	44
methyltriphenylphosphonium bromide	231–233	ethylene glycol	-12.9		-49.34	44
methyltriphenylphosphonium bromide	231–233	2,2,2-trifluoroacetamide	73–75		-69.29	44
benzyltriphenylphosphonium chloride	345–347	glycerol	17.8		50.36	44
benzyltriphenylphosphonium chloride	345–347	ethylene glycol	-12.9		47.91	44
benzyltriphenylphosphonium chloride	345–347	2,2,2-trifluoroacetamide	73–75		99.72	44
ZnCl_2	293	urea	134		9	21
ZnCl_2	293	acetamide	81		-16	21
ZnCl_2	293	ethylene glycol	-12.9		-30	21
ZnCl_2	293	hexanediol	42		-23	21

Table 3. Physical Properties of DESs, Ionic Liquids, and Molecular Solvents at 298 K^a

salt (mol equiv)	HBD (mol equiv)	viscosity/cP	conductivity/mS cm ⁻¹	density/g cm ⁻³	surface tension/mN m ⁻¹
ChCl (1)	urea (2)	632	0.75	1.24	52
ChCl (1)	ethylene glycol (2)	36	7.61	1.12	49
ChCl (1)	glycerol (2)	376	1.05	1.18	55.8
ChCl (1)	malonic acid (1)	721	0.55		65.7
C ₄ mimCl	AlCl ₃	19	9.2	1.33	
ChCl (1)	CrCl ₃ ·6H ₂ O	2346	0.37		77.3
C ₄ mimBF ₄		115	3.5	1.14	46.6
C ₄ mim(CF ₃ CO ₂) ₂ N		69	3.9	1.43	37.5
	ethanol	1.04		0.785	22.39

^aData taken from refs 1, 3, 13, 44.

in terms of their conductivity than other ionic liquids and molecular solvents. The origin of this disparity is proposed to be due to the large size of the ions and relatively free volume in the ionic systems. The viscosity of the ionic liquids is much higher than most common molecular solvents, and the change in viscosity with temperature is found to alter in an Arrhenius manner with large values for the activation energy for viscous flow. This was shown to empirically correlate to the ratio of the ion size and the average radius of the voids in the liquid¹³ (see section 2.3).

It is generally observed that there is a good linear correlation between the molar conductivity, Λ , of an ionic liquid and the fluidity (reciprocal of viscosity, η).²³ The same correlation is observed with DESs. This has previously been mistakenly attributed to the validity of the Walden rule, $\Lambda\eta = \text{constant}$. This is valid for a given electrolyte at infinite dilution in a range of solvents. Abbott showed that as a consequence of hole theory it is not the ions that limit charge transport but rather the holes which are at infinite dilution. Using this model it can be shown that the Nernst–Einstein equation is valid. The refractive index of choline chloride based liquids with the hydrogen bond donors glycerol, ethylene glycol, and 1,4-butanediol have been measured and compared to the predicted values using an atomic contribution method. It was found that it was possible to predict the refractive indexes of these liquids using the method chosen, where it was found that the refractive index lay between the values for the salt and the HBD.⁴⁵ Unsurprisingly, with the relationship between viscosity and temperature, it has been shown that the electrical conductivity of DESs is temperature dependent.⁴⁶ The effective polarity of choline chloride combined with four HBDs, 1,2-ethanediol, glycerol, urea, and malonic acid, has been predicted, and all four liquids were found to be fairly dipolar.⁴⁷

2.3. Hole Theory and Ionicity

The use of deep eutectics has in some cases been limited by their increased viscosity and hence reduced conductivity when compared to aqueous electrolytes. Few studies have been carried out to comprehend the fluid properties of either conventional ionic liquids or DESs. However, numerous models have been developed to account for the motion of ions in high temperature ionic liquids (molten salts), on the basis of the observation that the liquid volume and free volume of the liquid increase upon melting. The motion of ions in DESs has been rationalized using physical properties in hole theory.^{48–50,41} Hole theory assumes that, on melting, ionic material contains empty spaces that arise from thermally generated fluctuations in local density. The holes are of random size and location, and undergo constant flux. The

radius of the average sized void (r), is related to the surface tension of the liquid, γ , by

$$4\pi(r^2) = \frac{3.5kT}{\gamma} \quad (2)$$

where k is the Boltzmann constant and T the absolute temperature.

The average size of the holes in molten salts is of similar dimensions to that of the corresponding ion, so it is relatively easy for a small ion to move into a vacant site, and accordingly, viscosity of the liquid is low. However, the average size of holes will be smaller in lower temperature systems, coupled with a larger ion size this makes ion mobility difficult and explains why viscosities can be as high as 10^1 – 10^3 Pa.

To quantify the viscosity of DESs it is assumed that cavities are not formed, but simply exist and move in the opposite direction to solvent ions/molecules. At any moment in time, a fluid will have a given distribution of cavity sizes, and an ion will only be able to move if there is an adjacent cavity volume of suitable dimension. It is assumed that, at any moment in time, only a fraction of the solvent molecules are capable of moving, giving rise to the inherent viscosity of the fluid. The probability of finding an ion-sized hole in a high temperature salt is orders of magnitude larger than in its low temperature counterpart. By assuming the limiting factor in the viscosity of liquids is not the thermodynamics of hole formation, but the probability of vacancy location, then modeling fluidity becomes significantly easier. It was shown that accurate prediction of conductivity in ILs and DESs could be achieved.⁴⁸ Probability density and average size of free volumes within such liquids can be predicted using the Stokes–Einstein equation. The application of hole theory to modeling viscosity helps with the design of low viscosity DESs. To obtain optimum mobility the ions must be relatively small, but the liquid must contain large cavities. This can be obtained by producing a liquid with low surface tension and hence larger voids. This theory is also valid for ionic liquids with discrete anions.

Taylor et al. studied the diffusion of modified ferrocenes in imidazolium ionic liquids, and analysis of the data showed that the diffusion coefficient did not obey the Stokes' equation, but rather there was a significant change in the calculated radius with temperature.⁵¹ This was explained in terms of the size of the holes in the liquid, and it was shown that mass transport occurred by a hopping mechanism. This was confirmed by Mantle et al., who describe the first pulsed field gradient nuclear magnetic resonance (PEG-NMR) study of DESs.⁵² The molecular equilibrium self-diffusion coefficient of both the choline cation and hydrogen bond donor was probed using a standard stimulated echo PFG-NMR pulse sequence. The authors

illustrated that increasing the temperature led to a weaker interaction between the choline cation and the corresponding HBD. The findings also highlighted that the molecular structure of the HBD can greatly affect the mobility of the whole system. In ChCl:EG, ChCl:glycerol, and ChCl:urea the choline cation diffuses more slowly than the associated HBD, reflecting the trend of molecular size and molecular weight. The opposite behavior is observed for ChCl:malonic acid, where the malonic acid diffuses more slowly than the choline cation; the authors attributed this to the formation of extensive dimer chains between malonic acid molecules, restricting the mobility of the whole system at low temperature.

2.4. Electrochemical Behavior

In electrochemical applications, the behavior of electrolytes at an electrified interface is an important property; Silva et al. have investigated the electrochemical properties of ChCl based DESs. The properties of the interfaces between platinum, gold, and glassy carbon electrodes and a ChCl: glycerol DES were assessed using cyclic voltammetry and electrochemical impedance spectroscopy.⁵³ The double layer differential capacitance, obtained from electrochemical impedance, revealed that the capacitance curve of the ChCl:glycerol DES depends on the material of the working electrode. The values of capacitance were within the range of values reported for RTILs and have a similar shape dependence on the applied potential. The work revealed that differential capacitance increased with temperature in contrast to high temperature molten salts for all the electrodes examined with the exception of Au, where a crossing point in the capacitance curves was observed. The electrical interfaces of six different DESs based on choline chloride with 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, urea, and thiourea or acetylcholine chloride with urea were studied at a Hg electrode.⁵⁴ The CVs (Figure 4) did not show any current peaks which could be attributed to charge transfer processes within the potential limits chosen. In the ChCl:urea DES a pair of sharp peaks was observed around 0 V, similar to those observed for aqueous thiourea solution on Hg. After further investigation the authors tentatively attributed this to the formation of a film at the surface of the Hg electrode. The negative limit of polarization was

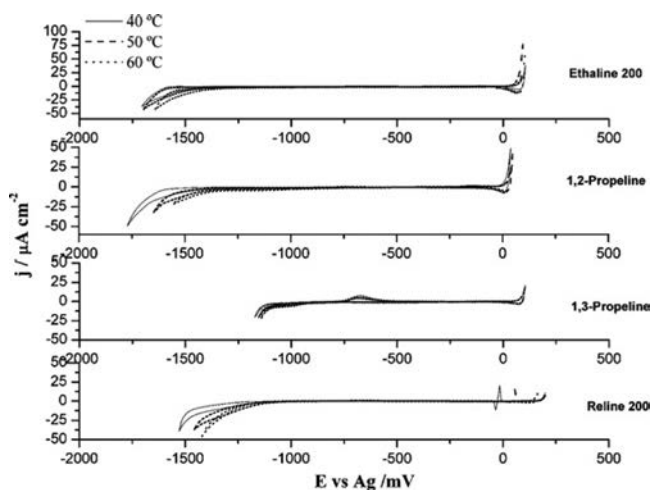


Figure 4. CVs of four DESs at a Hg working electrode: ethaline (1 ChCl:2 ethylene glycol), 1,2-propeline (1 ChCl:2 1,2-propanediol), 1,3-propeline (1 ChCl:2 1,3-propanediol), and reline (1 ChCl:2 urea) at 40, 50, and 60 °C (50 mV/s). Reproduced with permission from ref 54. Copyright 2010 Elsevier.

observed to be dependent on the hydrogen bond donor with the limit increasing in the following order: 1,3-propanediol < urea < ethylene glycol < 1,2-propanediol. Increasing temperature of the DES increased the observed capacitive current and decreased the electrochemical window. While the electrochemical windows of these liquids are not as large as in some conventional ionic liquids, they are wider than one might expect from a protic solvent (which these essentially are). Even though the concentration of protons can be fairly high in these liquids, the reduction of protons is not observed which is consistent with the idea that the protons are strongly bound to the chloride ions.

The differential capacitance curves for ethaline (1 ChCl:2 ethylene glycol), 1,2-propeline (1 ChCl:2 1,2-propanediol), 1,3-propeline (1 ChCl:2 1,3-propanediol), and reline (1 ChCl:2 urea) were nearly identical (Figure 5). The capacitance is constant at potentials negative of the point of zero charge (pzc). Replacing the diol hydrogen bond donor with urea only caused a change in the differential capacitance curves at a potential close to 0 V. The authors suggest that, similar to aqueous or organic electrolytes, at large negative potentials the structure of the interface comprises a layer of choline cations separated from the electrode surface by a layer of HBD molecules. As the potential becomes less negative the capacitance rises steeply suggesting the replacement of choline cations by the adsorption of anions. The minor effect of the HBD on the differential capacitance suggests

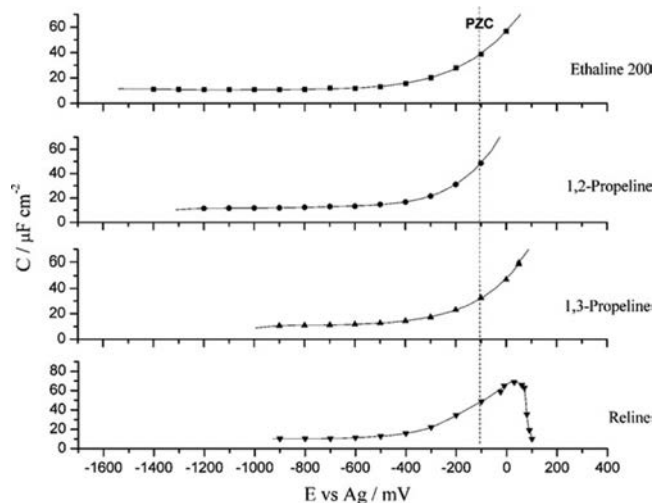


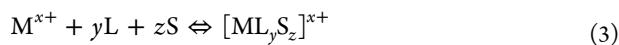
Figure 5. Differential capacitance curves measured at a Hg working electrode in ethaline (1 ChCl:2 ethylene glycol), 1,2-propeline (1 ChCl:2 1,2-propanediol), 1,3-propeline (1 ChCl:2 1,3-propanediol), and reline (1 ChCl:2 urea) at 60 °C. Reproduced with permission from ref 54. Copyright 2010 Elsevier.

the anion absorbed is mainly the chloride anion which is uncoordinated to the HBD. Replacing the choline with the acetylcholine cation (or replacing urea with the HBD thiourea) does not cause any change in the capacitance at large negative potentials. These results were taken by the authors as further support for a Helmholtz type layer model of the double layer at large negative potentials, comprising choline cations separated from the electrode surface by a layer of HBD molecules.

One of the critical issues is at which composition do DESs start to lose their ionic character and become predominantly a salt dissolved in a HBD. Abbott et al. proposed that DESs became more like ionic solutions when charge transport became ion-dominated rather than hole-dominated. The authors defined that

adherence of data to the Nernst–Einstein equation showed that charge carriers are at infinite dilution; i.e., they are holes. Once the concentration of salt fell below 20 mol % the molar conductivity was significantly above that predicted showing that ions dominated charge transport.⁴¹

Many of the applications in which DESs are currently employed involve the dissolution of metal ions in the liquid; it is therefore vital to understand how these metal ions behave when dissolved in a DES. Deviations from ideal behavior are notoriously difficult to characterize in molecular solvents. Abbott et al. have used equilibrium electrochemical measurements to determine activity coefficients for metal salts in DESs and ascertained how these vary with concentration.⁵⁶ In principle there is no difference in the way in which metal ions (M) behave in DESs and any molecular solvent (S). The metal ion interacts with whatever ligands (L) are available, and the equilibrium constant and hence species present are dependent upon the concentration of salt in solution and the relative Lewis or Brønsted acidity.



For most systems the solvent species is neutral and a relatively weak ligand. The chemistry of ligands in water naturally dominates, and the activity of the ligand is controlled by the ligand–solvent interaction. However, in a DES the solvent species that dominates complexation is the anion which has a significant Lewis basicity, as it is usually present in 5–10 mol dm⁻³ concentration meaning that, generally, even strong ligands can be displaced.⁵⁵

An understanding of the activity of a solute in solution is vital for utilizing the full potential of a reactive species. Abbott et al. studied the activity of silver ions, copper ions, and protons in ChCl:EG. Plotting E versus $\ln(m)$ they were able to prove that the change in the redox potential with molality for all three solutes obeys the Nernst equation for an ideal solution:

$$E = \frac{RT}{nF} \ln \left(\frac{m_1 \gamma_1}{m_2 \gamma_2} \right) \quad (4)$$

Here E is the equilibrium redox potential, R is the gas constant, T is the absolute temperature, F is the Faraday constant, n is the number of electrons, m is the molality of the solute, and 1 and 2 refer to the reference and test cells, respectively. The Ag/Ag⁺ and Cu^{2+/+} redox couple shows close to ideal behavior, suggesting that the ionic matrix shields the metal ions from each other, ensuring that they behave independently. Using a standard DES hydrogen electrode as a reference point, Abbott et al. were able to calculate a standard redox potential for the Ag^{+/0} and Cu^{2+/+} system, +0.034 and +0.58 V, respectively. The disparity from the aqueous standard redox potentials was attained to the difference in speciation of the metals in the two solvent systems. The observed ideal behavior through Coulombic shielding in DESs reinforces the hypothesis that DESs behave like molten salts and can thus be considered as ILs.⁵⁶

An electrochemical series for the redox potentials of a range of metal couples has been developed for the 1 ChCl:2 ethylene glycol DES and compared to the analogous values in aqueous medium with the internal reference [FeCN₆]^{3-/4-}.⁵⁷ Formal potentials were determined using 20 mM of the metal salt, and appropriate compensation was made for concentration and small temperature differences using the Nernst equation. Couples involving oxophilic p-block elements such as Ga and Sb showed the largest positive deviations from the line of equivalence. The

largest negative deviations were observed for couples of the chlorophilic late transition elements including Ag, Pd, and Au. These correlations and deviations were explained by speciation effects in the high chloride environment of the DES. This medium tends to stabilize the higher oxidation states of the chlorophilic late transition metals and destabilize those of the oxophilic p-block elements, increasing and decreasing the formal potentials, respectively. Interestingly, iodine is a stronger oxidizing agent in the 1 ChCl:2 ethylene glycol DES than in water. Molecular I₂ has a low solubility in aqueous media in contrast to many DESs; this permits the chemical oxidation of elemental metal by dissolved I₂ which can be exploited in metal processing, separation/recovery, and recycling technologies.

2.5. Speciation

The ionic nature and relatively high polarity of DESs mean that many ionic species, such as metal salts, show high solubility. One of the key questions when considering the reactivity of a metal in a DES is the species that form upon dissolution. Metal ions being generally Lewis acidic will complex with Lewis or Brønsted bases to form a variety of complexes. In aqueous solvents, the chemistry of H⁺ and OH⁻ dominate the species formed in solution, the redox properties, and the solubility of metals. The study of metal ion speciation in DESs has only started recently; unfortunately, the systems are more complex than aqueous solutions because of the differing Lewis basicities of the anions and composition of the eutectic. It is vital to understand speciation in DESs when trying to determine the mechanisms of nucleation and growth of metallic coatings, because the number and binding constants of the ligands determine the detailed mechanistic steps associated with electrochemical reduction. One of the reasons speciation is poorly understood is the difficulty in acquiring quantitative structural data. Most metals form ionic complexes that are difficult or impossible to crystallize from solution, and of course evaporation of the solvent is not possible. A series of in situ techniques are required to assimilate metal ligation in solution.⁵⁵

X-ray absorption fine structure (EXAFS) arises from a modulation in intensity of the X-ray absorption edge by interference with photoelectrons backscattered from neighboring atoms. Fourier transformation provides a radial distribution function in real space within a radius of approximately 600 pm. EXAFS is element specific and shows the local arrangement around the excited element, even for low concentrations. To date EXAFS has been used to study ZnCl₂, CuCl₂, and AgCl in both ChCl:EG and ChCl:urea DESs. It was found that ZnCl₄²⁻ and CuCl₄²⁻ were present in the former solutions whereas the last liquid contained a mixture of AgCl₂⁻ and AgCl₃²⁻.^{58–60} While these results are intuitively consistent with the high Cl⁻ ion concentration (ca. 4.8 M) in both of these liquids, it suggests that the coordination chemistry of the zinc ions at the electrode surface controls the deposition mechanism and further complicates the elucidation of these processes. A study by do Nacimeno et al. used soft X-ray absorption spectroscopy to probe solute–solvent interactions in ChCl:urea mixtures with a nitrate salt.⁶¹ The authors experienced significant problems with the signal of the solvent, but were able to detect solute signals, and see spectral changes attributed to solvent–solute interactions. The differential spectrum obtained from subtraction of the spectra of sodium nitrate dissolved in DES with pure DES was almost the same of that of pure nitrate indicating no strong interaction between the choline cation and nitrate anion.

2.6. Green Credentials

Ionic liquids have been described as “green solvents” largely because of their low vapor pressure. However, this is a misnomer, and in recent years the toxicity and biotoxicity of ILs have been investigated which has proven that they are not inherently “green”.⁶² DESs may offer a “greener” alternative to many traditional ILs, but they are also not by definition “green”. With the above formulations describing in excess of 10^6 liquids, some DESs will be inherently nontoxic being composed of benign constituents. Types I, II, and IV eutectics all contain metal salts with their innate toxicity; however, type III eutectics can encompass a variety of amides and polyols such as urea, glycerol, ethylene glycol, fructose, and erythritol, etc., which have low inherent toxicity (some formulations can even be produced using food grade ingredients).

To date most of the applications of DESs have been focused in the area of metal finishing, and relative toxicity has to be compared with the aqueous mineral acids that they seek to replace. Matthijs et al. have carried out a study on the environmental impact of the DES based on choline chloride and ethylene glycol in electroplating applications.⁶³ Both components are nonharmful to the environment, and both are readily biodegradable, with the resultant DES also readily biodegradable. Hence, the main environmental impact for the process was found to be related to the presence of heavy metals in rinsing solutions and products formed during electrolysis due to incomplete current efficiency at the cathode and anode reactions. After surface treatment in the DES electroplating bath, a film of the bath solution will remain on the parts and on the rack or barrel. The bath solution also remains in cavities or gaps and is transferred into subsequent baths. Process solution lost in this way is termed drag-out. Drag-out leads to the consumption of the plating bath and is a source of pollutants in the rinsewater. Matthijs et al. found that drag-out was the most influencing parameter on the environmental impact of the process, as it was three times higher compared to classical solutions due to the higher viscosity of the DES. However, they state that the ethylene glycol:choline chloride based liquid was not harmful for the environment compared to most ILs, and rinsewater can be treated with ion exchange to remove any metals.

The same group has addressed the environmental impact of the byproducts produced from the system during electroplating in a separate paper.⁶⁴ The authors observed the formation of several decomposition products such as 2-methyl-1,3-dioxolane and proposed some possible mechanisms for their formation. A range of chlorinated products such as chloromethane, dichloromethane, and chloroform were also detected, though chlorine gas evolution was not observed at the anode. The presence of the chlorinated products was ascribed to the existence of Cl_3^- in the solution, which was observed photometrically. The presence of chlorinated products did give rise to a large environmental impact; however, it was shown that the presence of chlorinate compounds could be reduced by the addition of water and that formation of 2-methyl-1,3-dioxolane could be reduced by the addition of sacrificial agents.

DESs do have lower vapor pressures than most molecular solvents which decrease their emission to the atmosphere; however, they are partly miscible with water and could inevitably end up in the aqueous environment. For DESs to be truly “green” a method for recycling needs to be ascertained along with methods to remove DESs from aqueous environments. Matthijs et al. have investigated the use of pressure driven membrane processes, nanofiltration, reverse osmosis, and pervaporation as

possible techniques for the recycling of DESs.⁶⁵ In electro-deposition processes DESs are likely to end up in the rinsewater; in other applications, DESs will have to be separated from water or solvents, e.g., the production of zeolites, Suzuki coupling reactions, and cellulose processing. Separation of water from a DES could be achieved by evaporation; however, this is very energy consuming and requires higher temperatures, at which some DESs may decompose.

Although components of a DES can be nontoxic and of low environmental impact. It does not necessarily follow that mixtures of these components will be non toxic and inherently “green”. This is underpinned by the fact the DESs have special properties that neither of the individual components have. The toxicity and cytotoxicity of choline chloride with the HBDs glycerine, ethylene glycol, triethylene glycol, and urea have been investigated by Hayyan et al.^{66,67} They found that the cytotoxicity of the DESs was much higher than their individual components and the toxicity and cytotoxicity varied depending on the structure of the components. It is clear that more investigation is needed into the toxicity of DESs before they can truly be claimed as nontoxic and biodegradable.

Deep eutectic solvent technology has been applied to a wide-ranging area of research topics from the lubrication of steel/steel contacts;⁶⁸ to an alternative electrolyte to water, or conventional organic solvent for the study of electronically conducting polymers;⁶⁹ to their use in analytical devices for the recognition of analytes such as lithium and sodium ions,⁷⁰ synthesizing drug solubilization vehicles,^{71,72} an electrolyte for dye-sensitized solar cells,⁷³ and the DES-assisted synthesis of hierarchical carbon electrodes for capacitors.⁷⁴ The major research effort to date has been concentrated on replacement solvents for metal finishing applications; however, in the past few years the number of groups investigating the potential of DESs as alternative solvents for organic synthesis has also increased, and hence, the output of papers in this area is also increasing.

3. METAL PROCESSING APPLICATIONS

The traditional electrofinishing industry is based on aqueous systems because of the high solubility of electrolytes and metal salts in water, resulting in highly conducting solutions. However, the technology is not ideal, water has a relatively narrow potential window, and so the deposition of some metals is hindered by poor current efficiencies and/or hydrogen embrittlement of the substrate. Further problems are faced by the industry with legislation due to limiting the applications of aqueous Cr, and the Co and Ni plating sector is becoming ever more affected by toxicity issues and the rising price of metals.

Currently, the major applications for DESs involve the incorporation of metal ions in solution for metal deposition, metal dissolution, or metal processing. The key advantages of using DESs over aqueous electrolytes are the high solubility of metal salts, the absence of water, and high conductivity compared to nonaqueous solvents. The potential windows of DESs are wider than aqueous solutions but less than some ionic liquids with discrete anions such as BF_4^- or $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$. Conventional ILs are not the focus of this review; comprehensive information and in depth analysis of electrodeposition in conventional ionic liquids are given in two reviews.^{75,83} As DESs are comparatively inexpensive when compared to conventional ILs and are much easier to produce in large scale batches, the scale-up and commercialization of DES based processes in the metal finishing and metal extraction industries have been, and still are, the subject of a number of EU and TSB

funded projects.^{76,77} The research involving metal processing has been divided into three broad topics in this review: metal electrodeposition, metal electropolishing, and metal extraction and the processing of metal oxides. The section starts by discussing metal electrodeposition where the greater part of the work in this area has been as an alternative medium for environmentally hazardous processes.

3.1. Metal Electrodeposition

Almost the entire electroplating sector is currently based on aqueous acidic or basic solutions although some specialist applications do use organic solvents,⁷⁸ but this is not commonplace. The industry has become adept at working around the constraints enforced by using water as a solvent. Zn, Ni, Cr, Co, Cu, Ag, and Au are all successfully plated with the use of brighteners and additives. More exotic metals can be deposited using plasma or chemical vapor techniques, allowing the coating of a wide range of substrates (metal, plastic, glass, ceramic, etc., with metals, alloys, or composites). The major issue with this technique is the high capital investment and running costs that have limited it to niche markets and high value products. Ideally, electroplating solutions should be low cost, nonflammable, have high solubility of metal salts, high conductivity, low ohmic loss and good throwing power, high rates of mass transport, and high electrochemical stability. As discussed above, the main limitations of aqueous based systems are their electrochemical stability; limited potential windows result in gas evolution leading to hydrogen embrittlement, and passivation of substrates, electrodes, and deposits. DESs have a high solubility for metal salts; unusually, this also includes metal oxides and hydroxides, which gives these systems an advantage over aqueous and organic based electrolytes. Passivation is often a problem in aqueous solutions due to formation of nonsoluble oxides and/or hydroxides on the surface of the electrode which inhibit the deposition of the target metal and can cause problems when thick metal films need to be deposited. Thicker metal films can be more easily deposited in DESs because the passivation effect is not observed due to the high solubility of metal oxides and hydroxides in DESs. The need for hazardous complexing agents (such as cyanide) in aqueous solvents causes a problem for the electroplating industry due to legal restrictions because of the inherent toxicity associated with the additives and the often high disposal costs. Water is not inherently a green solvent; although it is nontoxic, all solutes must be removed before it is returned to the watercourse.⁷⁹

Although it may be difficult to compete economically with existing plating systems for common metal applications, DESs can provide suitable media for the many technological goals of the industry.^{80,81} The replacement of environmentally toxic metal coatings, deposition of new alloys and semiconductors, and new coating methods for the deposition of corrosion resistant metals such as Ti, Al, and W^{82–84} have the potential to all be achieved in suitable DES systems. DESs may offer practical solutions to circumvent legal restrictions to technologically important plating systems such as Ni, Co, and Cr where many of the aqueous precursors are known carcinogens.

A range of metal reduction processes have been studied in DESs, including Zn,^{85,86,83} Sn, Cu,^{59,87} Ni,⁹⁶ Ag,⁶⁰ Cr,¹¹ Al,⁸⁸ Co,⁸⁹ and Sm.⁸⁹ Metal deposits can be obtained under either constant current or constant voltage regimes, and the morphology and adhesion of the deposit are often strongly dependent on current density, as observed in aqueous electrolytes; the morphology of metal deposits can also be tuned by

varying DES composition and using additives. Five metal deposition processes have been studied in considerable detail or are worthy of detailed discussion: chromium, aluminum, copper, nickel, and zinc. Each of these highlights different aspects of metal ion behavior which are different from aqueous solutions and need to be considered in large scale applications. DESs are now emerging as suitable media for the shape-controlled synthesis of nanoparticles which could be key in applications such as electrocatalysts, electrochemical sensors, air batteries, and fuel cells.

3.1.1. Chrome Plating. Hard chromium deposition using hexavalent chromium is a mature industry with technology highly optimized. There is however one stumbling block: the toxicity of hexavalent chromium is a significant concern and soon due to be limited by legislation. There are some Cr^{III} processes on the market, but trials with the less toxic trivalent chrome salt have had variable results. The electrodeposition of chromium (see Figure 6) from a dark green, viscous DES formed between

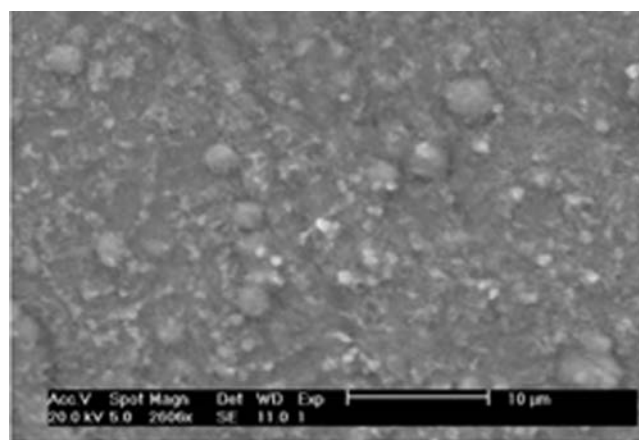


Figure 6. SEM image of a chrome deposit formed following the electrolysis of 1:2 $\text{ChCl}:\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ at 60 °C for 2 h onto a nickel electrode at current density of 0.345 mA cm^{-2} (bar = 10 μm). Reproduced with permission from ref 11. Copyright 2005 Wiley.

choline chloride and the trivalent chrome salt, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, has been reported.^{11,90} A hydrated metal salt is used, but this is not a concentrated aqueous solution as all the water molecules are either coordinated to the chrome center or associated with the free chloride ions; subsequently, the activity of water is low, and the process can be operated at very high current efficiency (typically >90%). Chromium coatings can be obtained in several morphologies by tuning the Cr(III) based electrolyte, for instance, dull black (soft, but not microcracked), dull gray metallic (hard >700 HV, increasing to 1400–1500 HV upon heat treatment), or mirror bright (usually very thin). These coatings have different applications as replacement technologies for Cr(VI) electrolytes in thermal, wear resistant, and decorative coatings. The addition of LiCl to the $\text{ChCl}:\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ mixture was found to allow the deposition of crack free, nanocrystalline black chromium films which gave good corrosion resistance.⁹¹

3.1.2. Aluminum Plating. The electrodeposition of Al is an important technological target as it has not been possible from aqueous electrolytes. It is the stability of the oxides of corrosion resistant materials that make the metals difficult to extract from minerals and apply as surface coatings. Al electroplating is currently carried out commercially using organic solvents in the SIGAL-process; however, the combination of toluene and

triethylaluminum makes this electrolyte highly flammable and pyrophoric so an alternative electrolyte would be welcomed by industry. A lot of research has been focused on the deposition of aluminum from conventional ILs, but the hygroscopic nature of AlCl_3 based ILs has delayed the progress in their use in many applications since they must be prepared and handled under inert gas atmosphere.⁹²

Al deposition has been achieved using type I eutectics, but the anodic reaction was slow and rate limiting. Recent developments using type IV eutectics have demonstrated that it is not necessary to have a quaternary ammonium cation in order to plate Al.⁸⁸ The anodic reaction is still slow and needs to be addressed to increase deposition rate, but the potential of this liquid is that just by adding a simple amide to AlCl_3 an electrolyte is formed that is relatively insensitive to water. Characterization of the liquid shows it to contain both anionic and cationic aluminum containing species, $[\text{AlCl}_2\cdot\text{urea}]^+$ and $[\text{AlCl}_4]^-$, and it is a suitable medium both for the electrodeposition of Al metal and the acetylation of ferrocene.

3.1.3. Copper Plating. Popescu et al. have electrodeposited Cu from CuCl_2 dissolved in ChCl combined with the hydrogen bond donors: urea, malonic acid, oxalic acid, and ethylene glycol.⁹³ To assess which DES was most suited to Cu plating the subsequent copper deposits were compared using optical microscopy and X-ray diffraction (XRD). Of the four DESs studied it was found that better deposits, i.e., fine, homogeneous, and adherent deposits, were obtained in ChCl:oxalic acid and ChCl:ethylene glycol. Murtomaki et al. have studied the electron transfer kinetics of the $\text{Cu}^+/\text{Cu}^{2+}$ redox couple using chronoamperometry, cyclic voltammetry, and impedance spectroscopy in ChCl:ethylene glycol.⁹⁴ The reaction was found to be quasireversible, and the authors reported the metal species present to be Cu^+ and Cu^{2+} , determined using UV-vis spectroscopy; the prevailing Cu^+ complex was found to be $[\text{CuCl}_3]^{2-}$ and that of Cu^{2+} $[\text{CuCl}_4]^{2-}$. Pollet et al. have reported the effects of ultrasound at different powers and frequencies on the electrodeposition of CuCl_2 in both aqueous KCl and ChCl:glycerol.⁹⁵ The authors demonstrated that the deposition of copper was greatly affected by ultrasound in both solvents, with a 5-fold increase in the current observed in ChCl:glycerol compared to silent conditions, i.e., when ultrasound was not applied.

3.1.4. Nickel Plating. Recent studies have demonstrated the electrolytic deposition of nickel from nickel chloride dihydrate dissolved in ChCl:urea and ChCl:ethylene glycol.⁹⁶ The deposition kinetics and thermodynamics were found to differ from the aqueous process, resulting in different deposit morphologies. Bright metal coatings were obtained by adding the brightening agents ethylenediamine (en) and acetylacetonate (acac), and deposits were put directly onto substrates such as aluminum without prior treatment. Guo et al. have tailored nickel coatings by electrodepositing onto copper from a ChCl:urea DES containing nicotinic acid.⁹⁷ The affect of nicotinic acid on the voltammetric behavior of Ni(II) was investigated, and it was found that nicotinic acid inhibited Ni deposition, acting as a brightener, producing highly uniform and smooth Ni deposits.

Thermochromic solutions (i.e., solutions that reversibly change color in response to heating and cooling) have been prepared by Gu et al. by dissolving transition metal chlorides such as $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, FeCl_3 , and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ in ChCl:ethylene glycol or ChCl:urea.⁹⁸ It was found that only $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ exhibited significant, stable, thermochromic behavior over a wide temperature range. The color of 0.1 M $\text{NiCl}_2\cdot$

$6\text{H}_2\text{O}$ dissolved in DES changed from pale green (room temperature), to spring green ($\sim 70^\circ\text{C}$), to blue ($\sim 120^\circ\text{C}$). Incorporating the Ni containing DES into a microporous PVDF film produced a thermochromic PVDF composite film for application in high performance thermochromic materials. The same authors published some interesting work using DESs to fabricate nanostructured Ni metal films⁹⁹ using constant voltage, pulse voltage, and reverse pulse voltage. A variety of nanostructured Ni films were produced with micro/nanobinary surface architectures such as nanosheets, aligned nanostrips, and hierarchical flowers (see Figure 7). Electrochemical measure-

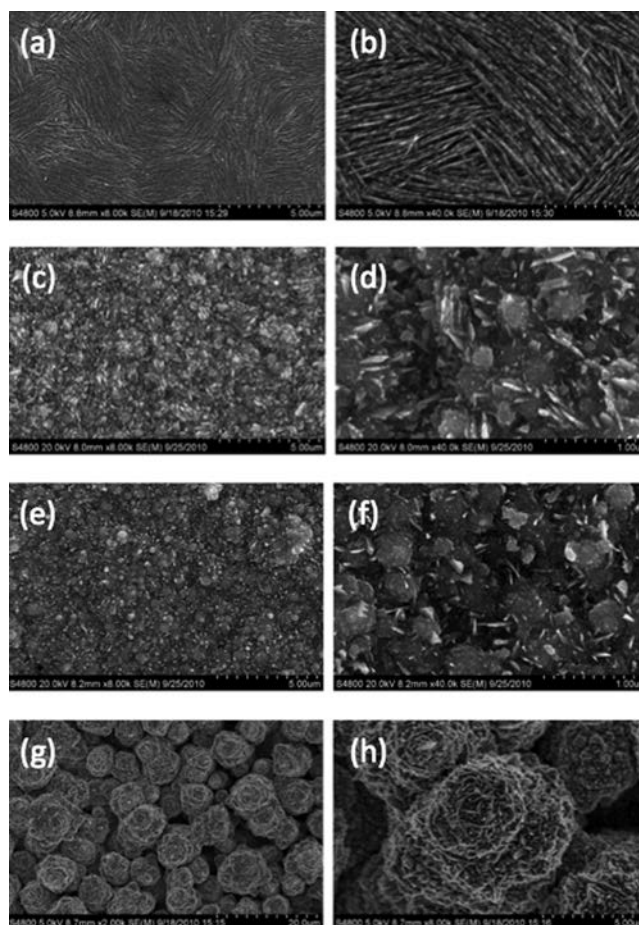


Figure 7. SEM images of different morphologies (nanosheets, aligned nanostrips, and hierarchical flowers) of Ni films deposited at 90°C by pulse voltage mode (a–f) and reverse pulse voltage mode (g, h). Reproduced with permission from ref 99. Copyright 2011 American Chemical Society.

ments revealed that the superhydrophobic Ni films exhibited an obvious passivation phenomenon, which may provide enhanced corrosion resistance in aqueous solutions.

3.1.5. Zinc Plating. Zinc is fundamentally important to the metal finishing industry primarily because of its environmental compatibility, cost, and corrosion protection properties. The deposition of metals such as Zn that are both inexpensive and lightweight offers valuable technological advances for energy storage applications. While the aqueous plating systems are clearly advanced and produce very good coatings, the study of zinc deposition in DESs has important implications for the production of zinc alloys. It is important to note that Zn metal deposited from DESs tends to have a compact microcrystalline

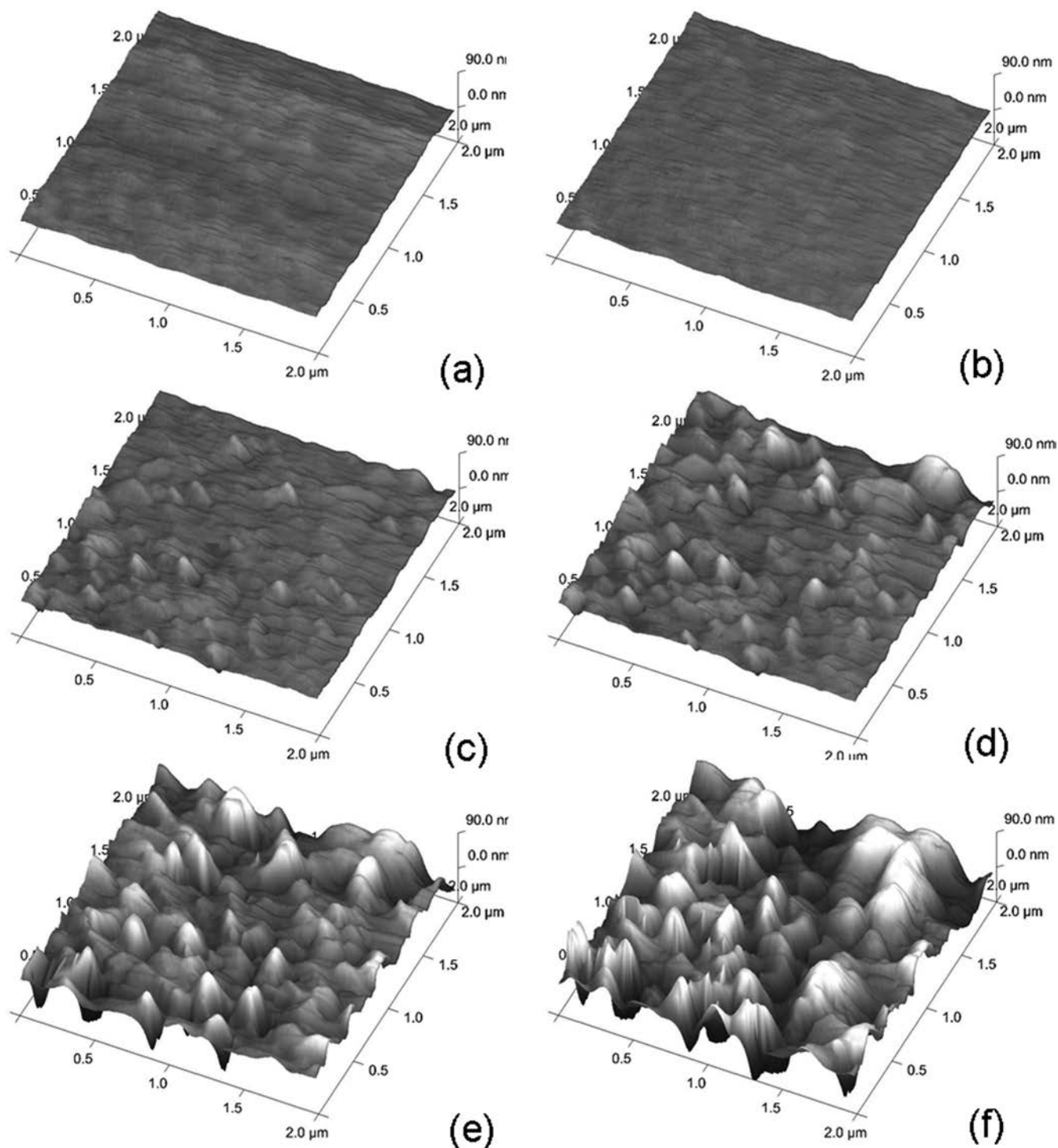


Figure 8. Tapping mode, liquid AFM images recorded in a 0.3 M ZnCl_2 solution in ethaline of an Au coated resonating quartz crystal under electrochemical control (-1.1 V vs Ag wire). Images show Zn deposition at times: (a) $t = 0$ s (i.e., bare electrode), (b) $t = 120$ s, (c) $t = 240$ s, (d) $t = 360$ s, (e) $t = 480$ s, and (f) $t = 600$ s. Reproduced with permission from ref 101. Copyright 2009 American Chemical Society.

structure, in contrast to Zn deposited from aqueous electrolytes which tends to have a dendritic structure in the absence of strong base additives. Deposition of Zn from DESs has been developed recently by PolyZion¹⁰⁰ which is an integrated FP7 project that is developing a novel fast rechargeable zinc polymer battery with a DES electrolyte for use in electric and hybrid electric vehicles.

Abbott et al. observed that the inclusion of certain nitrogen based chelating agents in the electroplating solution markedly affects the morphology of the resulting deposit. In an attempt to

gain some structural data regarding metal ion speciation in DES they have begun to use EXAFS as an in situ probe. Transmission EXAFS of a 0.05 M ZnCl_2 solution in either a 2 ethylene glycol:ChCl or 2 urea:ChCl liquid shows a single peak in the FFT spectrum corresponding to one dominant species, which after numerical fitting and comparison to solid state structural data is unambiguously $[\text{ZnCl}_4]^{2-}$. The transmission EXAFS spectrum shows no change upon the addition of 3 stoichiometric equivalents of chelating agent. This strongly suggests that

changes in morphology of deposit after the addition of complexing agents are because of chemical processes that take place in the diffusion layer or at the cathode surface, rather than in the bulk.⁸⁵

The double layer effects on zinc nucleation have been studied by Ryder et al.⁵⁸ Zn electrodeposition in a ChCl:EG and ChCl:urea DES are not mass transport limited. Though the morphology of the deposit obtained from the two liquids differs: zinc deposited from the urea based liquid had a “rice-grain” morphology, with homogeneously sized crystallites, consistent with a rapid nucleation mechanism; while the ethylene glycol based liquid gave very thin platelets formed with the planar face perpendicular to the electrode surface.

Changing the concentration of the solute affected the physical properties of the liquids to different extents, although it did not affect the morphology of the metal deposited. The speciation of zinc was shown to be the same in both liquids: $[\text{ZnCl}_4]^{2-}$. Double layer capacitance studies showed differences between the two liquids which were proposed to be due to the adsorption of chloride on the electrode. The differences in zinc morphology were attributed to the blocking of certain crystal faces leading to deposition of small platelet shaped crystals in the glycol based liquid.

The nucleation and deposition of zinc from a ChCl:ethylene glycol liquid have been studied using time-resolved in situ liquid atomic force microscopy (AFM) while simultaneously recording chronoamperometric and acoustic impedance electrochemical quartz crystal microbalance measurements.¹⁰¹ Modeling of the chronoamperometric data recorded for the initial nucleation process of the same experiment suggests that nucleation initially occurs via a progressive mechanism (derived from the Scharifker and Hills equations). Crystallites of different sizes were clearly visible from the AFM images throughout the whole deposition period monitored, suggesting that sustained nucleation also occurs via a progressive mechanism (see Figure 8).

3.1.6. Other Metal Coatings. The fundamentals of silver electrodeposition have recently come under study. Gomez et al have considered the role of the chloride anion in the nucleation process of silver deposited from the 2 urea:choline chloride DES.¹⁰² The voltammetric and chronoamperometric studies both suggest that the deposition of Ag is a 3D nucleation and growth process under diffusion control. The authors believe that the presence of chloride inhibits the growth of the deposit by hindering uncontrolled directional growth leading to deposits with rounded grains at short deposition times. The first ever digital holographic microscope (DHM) images of metal nucleation and growth have been published comparing Ag deposition from 1 choline chloride:2 ethylene glycol and 1 choline chloride:2 urea. The authors show that the growth of the silver is strongly dependent on the hydrogen bond donor of the DES.¹⁰³ The electrochemical reduction of three silver salts, AgCl, AgNO₃, and Ag₂O, in choline chloride:ethylene glycol and choline chloride:urea has revealed that silver is electrodeposited via 3D nucleation with mass transport controlled growth. More dense deposits were observed for the urea based liquid, and EXAFS studies revealed that the anion of the solvent only affected the electrochemical behavior when it was still associated with the metal; for the three salts investigated this only occurred with Ag₂O.¹⁰⁴

An investigation into the effect of HBD on the electrochemical and morphological properties of electrodeposited tin has revealed that the choice of HBD does not significantly change the electrochemistry with tin nucleation being found to progress

via a 3D instantaneous process with growth controlled by diffusion.¹⁰⁵ Electrodeposition of magnesium metal has been possible from a liquid containing dimethylformamide and magnesium chloride hexahydrate. Cyclic voltammetry indicated that the reduction of Mg²⁺ was irreversible, and X-ray diffraction (XRD) revealed that the deposits consisted of Mg₂Cu and MgO, i.e., the coating produced an alloy with the substrate, copper.¹⁰⁶ The electrochemical behavior of selenium oxide in choline chloride:urea has been characterized revealing the deposition of Se metal on a gold electrode.¹⁰⁷ The physical and electrochemical properties of choline chloride:ethylene glycol and choline chloride:urea containing palladium have been recorded, with deposition and stripping peaks for Pd observed in cyclic voltammetry investigations. Subsequent galvanostatic electrodeposition of Pd from these liquids produced deposits of nodular Pd particles as observed by SEM.¹⁰⁸ The surface morphology of palladium deposits from choline chloride:urea are affected by the addition of nicotinic acid amide and by the method of plating; direct or pulse current. The optimized Pd deposit was obtained either by the presence of the additive or by the use of pulse plating; if the two were operated in conjunction they changed the microstructure of the deposit.¹⁰⁹

3.1.7. Alloy Coatings. While the deposition of zinc is technologically relatively simple, the deposition of zinc alloys is particularly difficult, due primarily to the differences in redox potentials of the alloying elements in aqueous electrolytes. In a DES the redox potentials of metals are shifted from the values expected for aqueous systems due to the formation of chlorometallate ions and the thermodynamic difference in their reduction compared to the hydrated metal ions. Depositions of Zn/Co and Zn/Fe alloys from aqueous solutions produce an anomalous alloy where the less noble Zn is preferentially deposited to the other metal. In DESs it is possible to deposit a variety of alloy compositions, allowing either metal to be predominant, depending on the relative concentrations of the metals and the applied deposition potential. Zn–Sn alloy coatings on mild steel substrates have been prepared using DESs based on choline chloride and ethylene glycol or urea.¹¹⁰ It was shown that zinc and tin can be electrodeposited from these solvents both individually and as alloys; in addition this demonstrates the ability to change alloy morphology and composition by judicious choice of DES. A range of deposit compositions have been produced with over 80% Zn content possible.

Zn based alloy coatings from DESs could be used to replace or improve a variety of coatings including the following: elimination of hydrogen embrittlement in Zn–Ni alloys for aerospace applications, deposition of high Zn content coatings with Sn, deposition of higher Fe content Zn–Fe alloys than achievable by aqueous systems and replacement of strong acids and alkalis or toxic complexants that are currently used in aqueous electrolytes, and deposition of Zn–Co alloys with higher cobalt contents with a view to producing magnetic materials.¹¹¹

Ni/Co/Sn alloys have been deposited as a possible active material for oxygen evolution in water electrolysis or as an anode material for lithium batteries.¹¹² Cu/In alloy films have been deposited onto a Mo surface to investigate their suitability in the production of photovoltaic devices. The films were deposited from the 1 choline chloride:2 urea DES and contained islands of pure indium at lower overpotentials but resulted in dendritic growth at higher overpotentials.¹¹³ Other alloys to be deposited from these liquids are Sm/Co,⁸⁹ Zn/Cu,¹¹⁴ Zn/Mn,¹¹⁵ Ni/Zn,¹¹⁶ Fe/Ni/Cr,¹¹⁷ Cu/Ga,¹¹⁸ and Co/Sm.¹¹⁹ Sm/Co alloy has

the potential to be a hard magnetic material, depending on the metal ratio. When cobalt and samarium are both present in $\text{ChCl}:2$ urea, codeposition occurs with different morphology and composition depending on the applied potential. Nodular cobalt-rich deposits were obtained at low deposition potentials, and fine grained samarium-rich deposits were obtained at more negative deposition potentials. Valles et al. have also gone on to investigate the electrodeposition of CoSm magnetic films and nanowires. Zinc–manganese alloys are attractive corrosion resistant coatings for ferrous substrates. Their deposition is problematic from aqueous electrolytes due to the reactive nature of manganese and its low reduction potentials. Manganese chloride and zinc chloride were dissolved by Wilcox et al. in $\text{ChCl}:2$ urea; without any additives, the deposits were powdery, adding the correct amount of boric acid increased the amount of manganese in the deposit and reduced the powdery nature of the deposit. The electrochemical deposition of Ga and Cu–Ga alloys from $\text{ChCl}:2$ urea was investigated by Steichen et al. to prepare CuGaSe_2 semiconductors for use in thin film solar cells as a possible way to lower the cost of production for photovoltaic devices.¹²⁰ The authors report the successful conversion of Cu–Ga precursor films into p-type CuGaSe_2 absorber layers, without the loss of gallium during annealing.

3.1.8. Composite Coatings. The incorporation of particulate material into metal coatings has become an area of technological interest to form a corrosion barrier, to reduce surface friction, to greatly increase the hardness of a metal, or to produce abrasion coatings. Abbott et al. have shown that suspensions of silicon carbide, alumina, or diamond in various ChCl based DESs are stable for long periods of time without gravimetric settling.⁵⁹ These suspensions are stabilized by the relatively high viscosities of the liquids. The electrolytic deposition of metal from these liquids in the presence of particulate of suspension results in the physical incorporation of the particles into the metal coatings.

Silver is widely used as a coating for electronic connectors; however, it is extremely soft, and wear can be a significant issue. Frisch et al. have described improved wear resistant silver coatings obtained from solution of AgCl in $\text{ChCl}:\text{EG}$.⁶⁰ Up to a 10-fold decrease in the wear volume was observed with the incorporation of SiC or Al_2O_3 particles. The size but not the nature of the composite particle changed the morphology and grain size of the silver deposit, and the addition of LiF was found to significantly affect the deposit morphology and improve wear resistance.

3.1.9. Immersion and Electroless Coatings. Catalytically activated electroless deposition uses a reducing agent in solution, whereas immersion deposition relies on the galvanic potential difference between the ions in solution and the substrate. Immersion or electroless silver coatings are widely used by the printed circuit board (PCB) manufacturing sector as a means of protecting the surfaces of copper conductors from aerobic oxidation. Silver is also oxidized by air; however, in contrast to copper oxide, the silver oxide still dissolves in the molten solder that is used to join electronic components to the conductors of the PCB. The current commercial process, aqueous acid based, uses a solution phase reducing agent (typically formaldehyde) as well as a heterogeneous catalyst such as colloidal Pd metal. The major drawback to the acid-based process is that there is a competitive reaction between silver deposition and copper etching. For high density PCB applications this results in the selective dissolution of small copper features and ultimately costly failures of the boards. An alternative DES Ag immersion

plating process has been developed on the basis of the displacement and deposition of Cu and Ag, respectively.^{121,122} Although copper is still being removed from the board, the etching rate is uniform and easy to control. Unlike the analogous coating from aqueous solution, the Ag deposition from a DES is sustainable without the use of a colloidal catalyst. This is a consequence of the porous morphology of the coating.¹²³ Test samples on PCB tokens have been produced using the DES based process (see Figure 9); these have performed well in solder tests and accelerated aging tests.¹²⁴ The process offers both functional and environmental benefits.

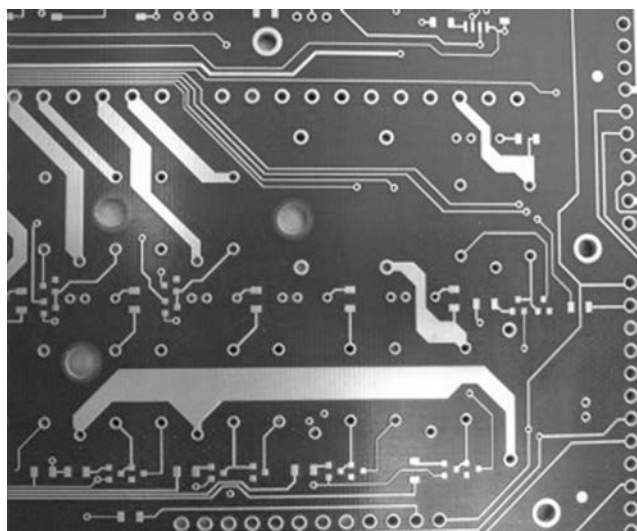


Figure 9. Printed circuit board (PCB) whose copper tracks have been coated with silver using the DES immersion process.

A new process has been developed for the immersion deposition of copper adhesion layers onto aluminum substrates.¹²⁵ The process is designed to facilitate electrolytic coatings of other metals on Al components. The process is obtained by simple immersion of the substrate in a DES containing Cu metal ions, and a thin, even, adherent, homogeneous film can be deposited in a few minutes. Electrolytic plating on top of the Cu layer is easily achieved using any conventional electroplating process: either aqueous or DES.

The ASPIS project is investigating the potential for using DESs as part of the electroless nickel and immersion gold (ENIG) deposition processes for PCBs.^{126,127,128} ENIG finishes for PCBs are widespread as they give excellent solderability that is retained after prolonged storage prior to assembly. However, there are a number of technical and reliability issues that can cause problems for PCB fabricators and their customers. The most common problem is “black pad”, caused by excessive corrosion of the Ni during the immersion Au process; the mechanisms that cause “black pad” are still poorly understood. One explanation is the galvanic corrosion of the nickel via protons in the acidic gold plating bath; the use of DESs could enable a neutral plating bath, minimizing the likelihood for corrosion to take place and reducing the possibility of “black pad” formation. The immersion Au process using DESs under development by ASPIS circumvents these issues.

3.2.10. Synthesis of Metal Nanoparticles. An interesting and emerging application of DESs is as a solvent for the shape-controlled synthesis of metal nanoparticles which could have a

large impact on the science of electrocatalysts. Gold nanoparticles were synthesized to produce Au based catalysts¹²⁸ without the use of any surfactants or seeds, but with a DES as the solvent. Star-shaped nanoparticles were successfully synthesized, directly from the reduction of HAuCl_4 by L-ascorbic acid at room temperature in the DES. Nanoparticles of various shapes and surface structure including snowflake-like and nanothorns were obtained by adjusting the water content of the DES. The electrocatalytic properties of the synthesized gold nanoparticles were tested using the electroreduction of H_2O_2 as a probe reaction; it was demonstrated that the star-shaped nanoparticles exhibited a much higher catalytic activity than other shaped nanoparticles and polycrystalline Au. Recently, the electrochemically shape-controlled synthesis of Pt nanocrystals with high surface energy has been demonstrated in a 1 ChCl:2 urea DES. The growth of concave tetrahedral nanocrystals was easily controllable without the need for seeds, surfactants, or other chemicals.¹²⁹

Pd nanoparticles assembled in a 2D superstructure have been electrodeposited from choline chloride:2 urea, and an anionic layer induced by adsorbed species has been observed with ultrasmall-angle X-ray scattering (USAXS).¹³⁰ Pt triambic icosahedral nanocrystals have been electrochemically synthesized from a choline chloride:urea DES, and when compared to a commercial Pt catalyst, they were found to have a higher electrocatalytic activity and stability toward ethanol electro-oxidation.¹³¹ A more environmentally friendly route to prepare CuCl nanocrystal powders for use as catalysts in organic synthesis has been reported using a DES.^{132,133} Spherical, magnetic nanoparticles of Fe_3O_4 have been prepared in choline chloride:urea and exhibited a better adsorption capacity for Cu^{2+} than for particles prepared in deionized water.¹³⁴

3.2. Metal Electropolishing

Electropolishing has been a subject of study since the process was first patented in 1930.¹³⁵ The principle of metal polishing is the controlled dissolution of a metal surface in order to reduce surface roughness and hence increase optical reflectivity. Electropolishing pieces increases corrosion resistance, decreases wear, and increases lubricity in engines, overcoming a major cause of failure. The majority of current commercial processes are based on aqueous phosphoric and sulfuric acid mixtures along with associated additives, such as CrO_3 . While the current commercial electropolishing processes are very successful, there are some major drawbacks: the solutions used are highly corrosive and toxic, and on a performance matter there is extensive gas evolution during the process that is associated with low current efficiency. Electropolishing with deep eutectic solvents has three main advantages over the commercial aqueous process: (i) Gas evolution at the anode/solution interface is negligible. (ii) Hence, high current efficiencies are obtained. (iii) Compared to the aqueous acid based solutions, the deep eutectic is benign and noncorrosive. Electropolishing has traditionally been successful for stainless steels, but in addition, the electropolishing of aluminum, titanium, Ni/Co alloys, and super alloys has been possible in DESs.

Stainless steel 316 can be electropolished using a DES based on choline chloride and ethylene glycol, which has freezing point of 10 °C (see Figure 10). The electrochemical response is significantly different from that observed in aqueous acid solutions; in the acidic solution the characteristic passivation response is observed at 1.3 V followed by what is believed to be a polishing region between 1.5 and 1.6 V. In the DES no



Figure 10. Stainless steel 316 polished (left) and unpolished (right).

passivation is observed; it is probable that the dissolution process is simply activation controlled. It was found that the formation of a passive oxide film at positive overpotentials was negated, allowing the efficient electro-dissolution of the stainless steel.¹³⁶ Alcohols such as glycerol have historically been used in aqueous electropolishing solutions as viscosity enhancers, but in general these solutions are thought to operate via a passivation of the metal surface. The ChCl:EG DES contains no chemical oxidizing agent and therefore should allow pure electrochemical control over the metal dissolution process without surface passivation. A highly polished surface can be obtained, without the use of any additives, with current densities between 71 and 53 mA cm^{-2} with an applied voltage of 8 V, at 40 °C.¹⁴ No gas evolution is observed suggesting that there are negligible side reactions occurring within the liquid. It was found that the DES with no additive had a current efficiency of 92%. This compares very favorably with aqueous based electrolytes where current efficiencies are $\sim 30\%$. Abbott et al. have published articles discussing the role of the surface oxide passivation layer on the polishing process and utilized atomic force microscopy (AFM) to gain insight into the nature and scale of morphological changes at the steel surface during the polishing process.¹³⁷

Electropolishing in deep eutectic solvents has mainly focused on stainless steel, but the electropolishing of aluminum, titanium, Ni/Co alloys, and super alloys has also been investigated. Ryder et al. have developed a new methodology for the removal of surface oxide scale from single crystal aerospace castings of nickel based superalloys (used in turbine blades) using anodic electrolytic etching with an ethylene glycol:choline chloride DES (see Figure 11).¹³⁸ This method enables the removal of scale from cast components, allowing the identification of defective parts before the expensive and time-consuming heat treatment process.

3.3. Metal Extraction and the Processing of Metal Oxides

The dissolution of metals and metal oxides is key to a range of important processes such as metal winning, corrosion remediation, and catalyst preparation and has recently been the subject of a review by Frisch et al.¹³⁹ The processing and reprocessing of metals is the source of a large volume of aqueous waste, with the treatment of acidic and basic byproducts being both energy and chemical intensive. RECONIF¹⁴⁰ is a project investigating DESs in the selective recovery of nickel from

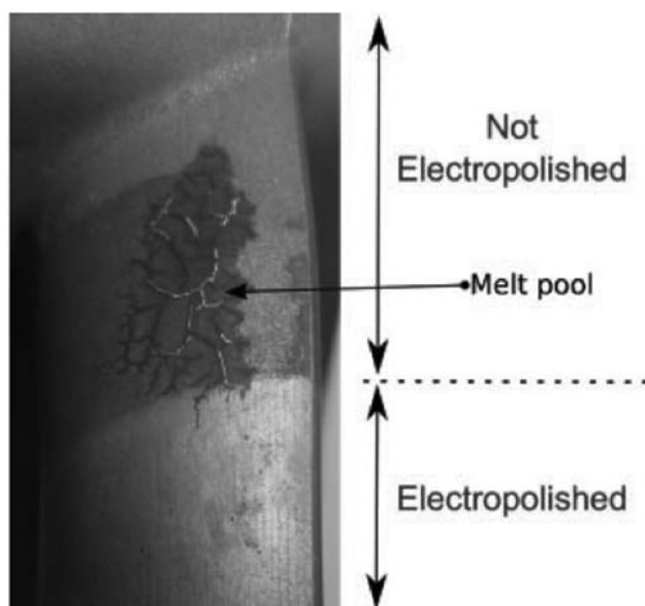


Figure 11. Blade aerofoil partially electropolished (lower section) and subsequently heat-treated. Surface melting is evident in the upper part of the aerofoil under the region of scale in the unelectropolished area. No evidence of scale or incipient melting in electropolished region. Reprinted with permission from ref 138. Copyright 2012 Maney.

different waste streams including filter cakes and battery waste. Most aqueous processes are based on either high temperature or hydrometallurgical methods, but are complex due to the diverse sources of starting materials such as metals, oxides, sulfides, carbonates, phosphates, silicates, and complex slags, sludges, and alloys. Metal oxides are insoluble in most molecular solvents and are generally only soluble in aqueous acid or alkali; the method used for extraction is dependent on the original matrix, the required purity, and the value of the end product. Following modern standards for environmental protection, all solutes must be removed before a solvent (normally water) is discharged to the environment; there are four main methods used to recover metals from solution: precipitation, ion exchange, electrodeposition, and cementation. Electrodeposition or electro-winning is the most commonly used technology for metals such as gold, silver, and copper. However, there are three major drawbacks to this process: the pH must be accurately maintained to control the deposition process; complexing agents such as ammonia or cyanide are used to control the solubility and deposition properties; and hydrogen gas and oxygen evolution can lead to embrittlement of the metal deposit, diminishing its quality and leading to low current efficiencies. Precipitation is another option, but usually results in deposits that are not the pure metal but salts such as hydroxides, sulfides, or carbonates. To recover aluminum and chromium they have to be chemically or electrochemically reduced in high temperature processes with high energy demands.

An increasing number of groups are now using ILs and DESs for solvatometallurgical processing; the advances made with DESs only are discussed here. Extensive studies have been performed on the solubility of metal oxides in a variety of deep eutectic solvents. Type III DESs have been shown to dissolve a range of metal oxides;¹⁴¹ ligands such as urea, thiourea, and oxalate are well-known complexants for a variety of metals and can be made part of the DES. Metals can be separated from a complex mixture using electrochemistry;¹⁴² however, on the

downside, these liquids are all totally miscible with water and cannot be used for biphasic extraction. The solubility of 17 metal oxides in the elemental mass series Ti through to Zn has been reported in three DESs based on choline chloride,¹⁴³ with judicious choice of the hydrogen bond donor leading to selectivity for extracting certain metals from complex matrices.¹³

In aqueous solutions, redox potentials can be selectively shifted by judicious choice of an appropriate ligand, while in principle the same could be achieved using the same ligands in DESs: the relative strengths of possible metal–anion complexes are largely unknown and remain an important parameter to quantify. Abbott et al. have recently developed the first comparable electrochemical series in two deep eutectic solvents.¹³⁹ The authors have shown that metals can be electrowon into their composite materials by using the difference in redox potentials of the metals in a model experiment using copper/zinc mixtures. Copper has a higher redox potential, and so it needs to be deposited first, the cathode can then be changed, the voltage increased, and zinc deposited. The authors also demonstrate the use of iodine as a stable, reversible electro-catalyst for the dissolution of a range of metals. The redox potential of I_2/I^- in a choline chloride:ethylene glycol DES was found to be more positive than that of most common metals and was shown to be able to oxidize and recover gold.

A hybrid DES of choline chloride, ethylene glycol, and urea has been utilized in the large scale extraction of lead and zinc from electric arc furnace (EAF) dust.¹⁴⁴ The DES showed selectivity in EAF dust toward just zinc and lead oxides, while iron and aluminum oxides were insoluble. The electrochemical series in DESs shows that Pb would be electrowon first over Zn; as Pb was not economically worth extracting it was cemented using Zn dust. Tests showed that Zn could be subsequently electrodeposited with a current efficiency of 75%. However, this is not economically efficient for such a relatively inexpensive metal; therefore, the most economically viable solution was to precipitate ZnCl using ammonia, filter off the precipitate, and boil away the ammonia, leaving behind the DES to be used again. A pilot plant was constructed to test the efficacy of using DESs for large scale metal extraction. Choline chloride:urea and choline chloride:malonic acid have been shown to be effective in the removal of copper oxides and fluorides from post etch residues,¹⁴⁵ and the malonic acid based liquid has also been successful in the removal of residues from the CF_4/O_2 etching of a copper coated DUV photoresist.¹⁴⁶ DESs have also shown promise in removing organic sulfides from fuels.¹⁴⁷

4. SYNTHESIS APPLICATIONS

Legislative control is encouraging the adoption of greener methodologies in chemical synthesis, and ILs have been heralded as a replacement for some more volatile organic solvents. However, the “green” credentials of ILs and DESs are still very much debated due to a shortage of toxicological studies. DESs have recently been proposed as environmentally benign alternative solvents for synthesis and have been considered in reviews on the subject;^{148,149} however, the possibility of using DESs as solvents for synthesis has not received as much focused research attention as utilizing DESs as alternative solvents for metal finishing applications. In order for this area of research to flourish, more substantial research needs to be carried out into the long-term environmental applications of using DESs to perform these synthetic procedures.

Abbott et al. initially developed DESs based on choline chloride and zinc chloride as inexpensive readily available

alternatives to ILs in synthesis. These ChCl-ZnCl_2 Lewis acidic solvents have been successfully employed for a variety of synthetic reactions including Diels–Alder cycloaddition, Fischer indole annulation, and polymerizations.^{150,151} Since these proof-of-principle experiments, other research groups have gone on to investigate the suitability of DESs in synthesis reactions, and work in this area is increasing. Shankarling et al. have utilized DESs for the selective N-alkylation of aromatic primary amines, avoiding the complexity of producing multiple alkylations which can occur with polar organic solvents and high reaction temperatures. The authors have compared two new “green” methods for the process: biocatalysis using the enzyme lipase and DESs as a catalyst and recyclable solvent, thus conducting the synthesis under mild conditions and without the use of a strong base or highly polar organic solvent. The model test reaction selected was the reaction of aniline and hexyl bromide. The lipase catalyst in an ethanolic medium gave the best results of the organic media screened giving the desired product. The DES ChCl:urea gave products in the same reaction time with good, only slightly lower, yields (see Table 4). The DES was able to be

Table 4. Influence of Organic Solvents and Biodegradable/DES Media for Mono-N-alkylation of Aniline with Hexyl Bromide in the Presence of Lipase Biocatalyst

	reaction time (h)	yield (%)
Organic Solvent Used in Conjunction with Lipase		
ethanol	4	85
chloroform	5	81
dichloromethane	6–8	75
hexane	12	50
DES or Biodegradable Media		
glycerol	10	55
ChCl:glycerol	8	65
ChCl:urea	4	78

recycled and reused at least five times.¹⁵² Choline chloride:2 zinc chloride has been used as the solvent for the preparation of primary amides from aldehydes or nitriles.¹⁵³

Shankarling et al. have also utilized a choline chloride:urea DES as catalyst and reaction medium for the bromination of 1-aminoanthra-9,10-quinone, eliminating the requirement for volatile organic solvents and concentrated acids as solvents or catalysts. The DES reduced the reaction time from 10 to 12 h for chloroform and methanol to 2–3 h with a high purity yield of 95% compared to 70–75%.¹⁵⁴ The DES was easily separated and reused without loss of activity. The same group has also reported the synthesis of cinnamic acid and its derivatives via a Perkin reaction in the same DES, choline chloride:urea.¹⁵⁵ Conventionally, cinnamic acid and its derivatives are prepared using benzaldehyde, acetic anhydride in the presence of a base at 180 °C; the drawbacks have been the use of strong bases, organic solvent, high reaction temperatures, long reaction times, and low yields. The reaction proceeded efficiently under mild conditions (a reaction temperature of 30 °C compared to 140 °C for the conventional method) without the need for an additional catalyst, with better yields compared to the traditional method (~30% increase in yield was observed for the same product synthesized with the DES method compared to the conventional method); again, the DES was able to be recovered and reused.

del Monte and Luna-Bárceñas et al. have demonstrated that a ChCl:acrylic acid or $\text{ChCl:methacrylic acid}$ DES has superior performance than organic solvents and ionic liquids for frontal

polymerizations.¹⁵⁶ Tailoring the viscosity of the DES allowed the front temperature and velocity to be controlled, enhancing polymer conversion (up to ca. 75% and 85% in the acrylic acid and methacrylic acid, respectively). del Monte and Gutiérrez et al. proved that a $\text{ChCl:ethylene glycol}$ DES was a suitable solvent for the polycondensation of resorcinol–formaldehyde gels to prepare carbons and carbon–carbon nanotube composites with conversion rates and carbon content in the range of and even slightly above those obtained in aqueous solutions.¹⁵⁷

Glycerol based DESs have been used as an easily prepared, biodegradable, and inexpensive alternative to conventional aprotic cation–anion paired ILs for the study of protease activation by Zhao et al.¹⁵⁸ Han et al. have reported the efficient conversion of fructose to 5-hydroxymethylfurfural (HMF) to produce liquid fuels.¹⁵⁹ The conversion of fructose to 5-hydroxymethylfurfural is a key step for using carbohydrates to produce liquid fuels and value-added chemicals. The authors tested a range of conventional ILs and DESs based on ChCl and compared their conversion selectivity and yield, with the best choline chloride based liquid displaying a conversion, selectivity, and yield all above 90%. DESs based on choline chloride and citric acid were found give the best all round results.

DESs have also been used in the development of a new synthetic route for polyoxometalate (POM) based hybrids.^{160,161} POMs have been synthesized by two methods, but both have drawbacks: in the traditional method the temperature of the reaction system cannot usually exceed 100 °C because of the boiling points of the solvents; the second method is hydrothermal or solvothermal synthesis which utilizes high temperature, high pressure environments to overcome solubility limitations in organic solvents. This method has been limited by low yields, insolubility of the final product, difficulty in repetition and control, and the potential explosion of organic solvent and organic reactants under the experimental conditions. A choline chloride:urea eutectic avoids the disadvantages of both these methods, removing the potential for explosion, and improving both solubility and yield. The selective preparation of α -mono or α,α -dichloro ketones and β -ketoesters¹⁶² can be performed at room temperature with a 86–95% yield in a choline chloride:p-TsOH DES in comparison to the traditional method using silica gel as the catalyst and methanol as the solvent under reflux with a 86–98% yield. A one-pot α -nucleophilic fluorination of acetophenones in a DES has been developed by Zou et al.¹⁶³ α -Fluoroacetophenones can be prepared from acetophenones through electrophilic or nucleophilic fluorination. A DES of ChCl and p-TsOH was formed, and three different methods using nucleophilic fluorination were used to try to produce α -fluoroacetophenones. The first and second method used KF or $\text{TBAF}\cdot 3\text{H}_2\text{O}$ as the fluorinating reagent, improving the yields of α -fluoroacetophenones as compared to those prepared from α -bromoacetophenones. The last method took advantage of the high chloride environment in the DES to synthesize α -fluoroacetophenones directly from acetophenones in pot, giving yields higher than some seen in electrophilic fluorination using N–F reagents.

The scope of the uses of DESs in synthesis is now widening. DESs have been used to catalyze a one-pot synthesis of nitriles from aldehydes,¹⁶⁴ 2*H*-indazolo[2,1-*b*]phthalazine-triones,¹⁶⁵ the synthesis of phenols,¹⁶⁶ and pyran and benzopyran derivatives.¹⁶⁷ DESs have been utilized in the Paal–Knorr reactions¹⁶⁸ and the synthesis of amino acid dithiocarbamates,¹⁶⁹ aurones,¹⁷⁰ xanthenes and tetraketones,¹⁷¹ dithiocarbamate derivatives,¹⁷² peptides,¹⁷³ 1,4-dihydropyridine derivatives,¹⁷⁴

3,4-dihydro-2(*H*)-pyrimidinones,¹⁷⁵ polysubstituted imidazoles,¹⁷⁶ and *N*-substituted pyrroles.¹⁷⁷

Interestingly, it has been suggested that DESs can be used as media for DNA and RNA based technologies, contradicting the argument that water is necessary for nucleic acid second structure to be observed. Hud et al. report that nucleic acids can form four secondary structures that reversibly denature with heating in a water-free urea based DES.¹⁷⁸ In some cases the nucleic acid sequences studied exhibited different relevant stabilities and different secondary structures compared to those observed in aqueous media. Owing to their anhydrous character and capacity to support natively folded DNA and protein structures, DESs are appealing media for the nonenzymatic synthesis of biopolymers. It has been shown that DNA is soluble in choline chloride in combination with the HBDs levulinic acid, glycerol, ethylene glycol, sorbitol, and resorcinol.¹⁷⁹

4.1. Ionothermal Synthesis

The use of organic templates (structure-directing agents, SDAs) is one of the most successful methods of preparing new inorganic materials^{180–182} such as zeolites, transition metal phosphates or oxides.¹⁸³ Crystalline porous solids are of interest in a number of areas of modern science, particularly those associated with catalysis and gas adsorption.¹⁸⁴ Traditionally, these materials have been produced by hydrothermal synthesis, where a templating agent is added to a molecular solvent; SDAs become enclosed in the crystallizing inorganic–organic hybrid material and define the molecular-size pore systems which become accessible after combustion of the SDA.¹⁸⁵ However, in 2004, Cooper et al. developed a novel method of preparing porous solids based on the use of deep eutectic solvents as both solvent and structure-directing agent (template),¹⁸⁶ see Figure 12. This

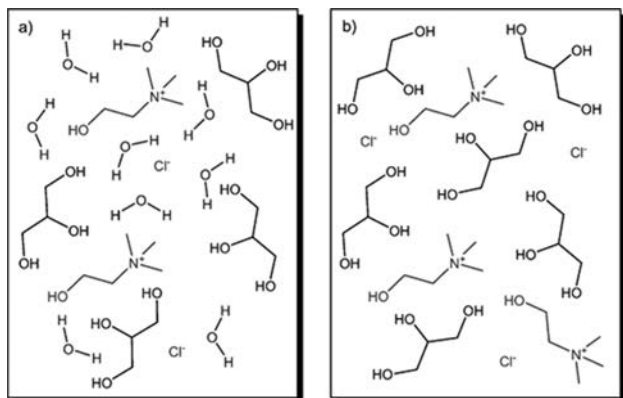


Figure 12. Schematic comparison between (a) hydrothermal synthesis where interactions between the excess solvent (water) and the template or framework dominate and (b) ionothermal synthesis where the template–framework interactions dominate.

new method, termed “ionothermal synthesis”, has some interesting features and potential advantages over the traditional methods of molecular sieve synthesis. Ionothermal synthesis uses ionic liquids as both the solvent and potential template (or structure-directing agent) simultaneously in the formation of solids. It directly parallels hydrothermal synthesis where the solvent is water. DESs unstable at high temperatures can be used as the media for ionothermal reactions. The organic template is not added to the mixture in the traditional manner, but delivered in a controlled approach by the breakdown of one of the components of the DES itself. Advanced ionothermal synthesis

allows the tuning of solvent properties of the DES to match the system requirements. Deep eutectic solvents have structures with a high degree of local order, relatively long-range spatial correlations and a three-dimensional distribution that reflects the asymmetry of the deep eutectic cations. The long-range asymmetric distribution comes from the long-range Coulombic interactions and could have major implications for structure direction in the synthetic process.¹⁸⁷

Ionothermal synthesis has many benefits over hydrothermal synthesis: most DESs have vanishingly small vapor pressures, which means autogenous pressure is produced on heating; in contrast, ionothermal synthesis can take place at ambient pressure, eliminating safety concerns with high solvent pressures. Potentially millions of eutectic mixtures are available compared to only ~600 molecular solvents used for hydrothermal synthesis, offering many more opportunities for the synthesis of new porous frameworks.¹⁸⁶ Finally, the use of DESs as solvent reduces the tendency for water to be accommodated in the resultant structure, even when there is a small amount of water present in the reaction mixture.¹⁸⁸

The Morris group at the University of St Andrews, U.K., is currently the main group of researchers working on ionothermal synthesis reactions, and in 2007 Parnham and Morris published a review of the early work carried out on the subject.¹⁸⁹ Recent publications using ionothermal synthesis have reported the formation of aluminum phosphate,^{190,191} cobalt aluminophosphate,^{192–195} zirconium phosphates,^{196–198} propylene diammonium gallium phosphate,¹⁹⁹ zinc phosphate,^{200,201–203} zinc and cobalt metal phosphites,²⁰⁴ and organic–inorganic hybrid materials.^{205–209} Also reported are a novel cobalt phosphate–borate compound²¹⁰ for use as nonlinear optic materials, lanthanide^{211,212} or nickel²¹³ metal organic frameworks for the ultrafast formation of ZnO mesocrystals,²¹⁴ reduced graphene oxide,²¹⁵ and hierarchical porous carbon monoliths.²¹⁶

4.2. Gas Adsorption

The adsorption and sequestering of CO₂ is a current hot topic aimed at reducing global warming. Great efforts are focused on developing energy sources that are not CO₂ emitting; however, these are not at the stage where they can be implemented on a large scale. The design of a sustainable synthetic process for the preparation of recyclable solid sorbents that exhibit an enhanced sorbent capability is vital. The use of DESs to prepare these materials appears promising in terms of efficiency and sustainability.^{217,218} Two groups in China and Spain have used ionothermal synthesis to produce porous frameworks suitable for CO₂ capture. Bu et al. have reported the synthesis of a series of metal–organic frameworks, some with promising gas storage capabilities.^{207,219,220} Gutierrez et al. have used a resorcinol:3-hydroxypyridine:choline chloride containing DES as the liquid medium, structure-directing agent, and the source of carbon and nitrogen to produce nitrogen doped hierarchical carbons.^{216,221}

Han et al. have reported the high catalytic efficiency of a ChCl:urea DES supported on molecular sieves for the chemical fixation of carbon dioxide to cyclic carbonates.²²² It was demonstrated that this new biodegradable and green catalyst was very active and selective and had the potential for synthesizing cyclic carbonates from CO₂ and epoxides. After the reaction the solid catalyst and products could be easily separated because the DES was insoluble in the products, and the catalyst was reusable. Porous carbon nanosheets synthesized in DESs with controllable thicknesses that can separate CO₂ from N₂ have been reported.²²³ DESs could also be utilized themselves as solvents

to capture CO₂.^{224–227} Choline chloride:lactic acid has been investigated as a solvent to capture CO₂, and the mixture was found to be easily tunable; however, the solubility of CO₂ was lower than other DESs studied in the literature.²²⁸ SO₂ is one of the main air contaminants emitted from burning fossil fuels; it has been found that ChCl:glycerol rapidly adsorbs SO₂, with an easy and fast release.²²⁹

4.3. Biotransformations

An emerging research area for DESs is their use in biotransformations. A biotransformation is a chemical modification made by an organism or enzyme on a chemical compound, and is vital to our survival as it allows the body to transform absorbed nutrients (food, oxygen, etc.) into substances that we require to function. The body also uses biotransformation or metabolism to turn an absorbed drug into the active agent or to convert toxins in the body into less harmful substances that can be excreted. Traditionally, biotransformations have been performed in aqueous solvents; however, biocatalysis has also been attempted in polar organic solvents such as acetone, methanol, or DMSO, although the polar organic solvents regularly denature enzymes. Replacing polar organic solvents with DESs allows substrates to dissolve without deactivating enzymes. DESs can be used in three different ways: as a cosolvent with water to help nonpolar substrates dissolve in aqueous solution, as a second phase in a water–DES mixture, or as a nonvolatile replacement for nonaqueous solvent. Deep eutectics propose to be a technically and economically viable alternative to organic solvents.^{230,231}

The first proof-of-concept concerning the use of DESs in biotransformations only appeared in 2008.²³² The reactions studied so far have involved lipase-catalyzed processes such as transesterification,^{232,233} aminolysis, epoxide hydrolysis,²³⁴ N-alkylation of aromatic primary amines,²³⁵ and Knoevenagel condensation reactions.²³⁶ These have generally exhibited rates and enantioselectivities comparable to or higher than those reported for conventional organic solvents. It has been recently discussed in the literature whether naturally forming DESs can provide the missing link in understanding cellular metabolism and physiology.²³⁷

Biotransformations using microorganisms are limited in any nonaqueous solvent, and adding water unfortunately modifies DESs, breaking the electrostatic interactions among the components. To overcome this, freeze-dried whole cells have been incorporated in a DES, preserving the bacteria integrity and viability. In 2008, Gutierrez and del Monte initially published the preparation of a DES in its pure state through the freeze-drying of aqueous solutions of the individual DES counterparts and went on to explore the suitability of freeze-drying to incorporate organic self-assemblies in the DES with the full preservation of their self-assembled structure.²³⁸ The strategy reported in this work was the freeze-drying of aqueous solutions containing the individual counterparts of the DES and the preformed liposomes (see Figure 13). In 2010 they published the proof of principle of the suspension of a bacterium (a strain of *E. coli*) in a glycerol choline chloride DES.²³⁹

4.4. Transformations of Unprotected Sugars, Cellulose, and Starch

Transformations of certain organic compounds such as unprotected sugars and cellulose can also be carried out advantageously in these liquids. The selective O-acetylation of sugar and cellulose²⁴⁰ has been reported, as well as the cationic functionalization of cellulose.²⁴¹ The O-acetylation of carbohy-

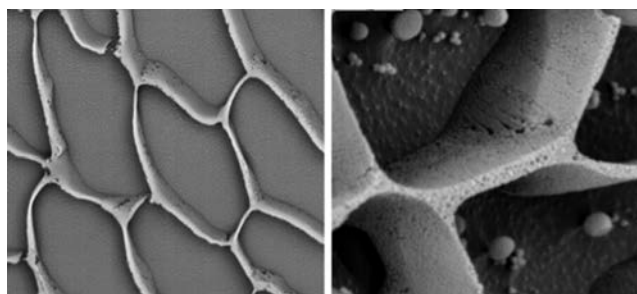


Figure 13. Cryoetch SEM micrographs of liposomes (ca. 200 nm diameter) suspended in urea:choline chloride (left, bar is 20 μm) and thiourea:choline chloride (right, bar is 2 μm). Reprinted with permission from ref 238. Copyright 2009 American Chemical Society.

drates is used for the protection of hydroxyl groups and for the purification and structural elucidation of natural products. DESs based on ZnCl₂ and ChCl are effective at carrying out O-acetylation reactions on a number of monosaccharides and cellulose. Per-O-acetylation was exclusively observed with monosaccharides and for low molecular weight polymer. Partial acetylation of cellulose was shown to be possible with some control over the degree of modification. The efficient cationic functionalization of cellulose was demonstrated in choline chloride:urea DES which acts as both solvent and reagent. It was shown that all the available hydroxyl groups on the cellulose had been modified. Jerome et al. have reported the rapid decrystallization of cellulose in DESs.²⁴² The authors discuss the effect of additives and the recycling of the DES. Starch is a biopolymer used in industry as a coating in paper, textiles, and carpets and in binders, adhesives, absorbants, and encapsulators. It is often modified to improve its end-use properties; however, the only solvent it is soluble in is dimethyl sulfoxide, and then only sparingly. Starch has been found to be soluble in choline chloride:oxalic acid and choline chloride:ZnCl₂, and as a result, these DESs could be used as a solvent for the chemical modification of starch.²⁴³

DESs have also been investigated for their suitability as plasticizers for starch^{244,245} and cellulose acetate.²⁴⁶ DESs based on choline chloride are good candidates for starch modification because they interact strongly with the OH groups of the glycosidic units, decreasing chain interactions and hence plasticizing the polymer. They can also wet the surface of individual grains and bind them together. The DES found to have the best plasticizing properties was ChCl:urea. ChCl:urea has been used to suppress the crystallinity of corn starch and cellulose acetate in a polymer electrolyte containing lithium bis(trifluoromethanesulfonyl)imide, LiTFSI. The highest ionic conductivity for corn starch was obtained from a sample containing 80 wt % of DES, with a calculated conductivity value of $1.04 \times 10^{-3} \text{ S cm}^{-1}$ in comparison with a sample containing 60 wt % DES for cellulose acetate, giving an ionic conductivity of $2.61 \times 10^{-3} \text{ S cm}^{-1}$.

4.5. Purifying and Manufacturing Biodiesel

There are many benefits of producing biodiesel as an alternative fuel: its synthesis from a natural product means that it is a carbon-neutral fuel; it produces significantly fewer particulates than conventional diesel fuel with no sulfurous emissions; and it can be used pure or blended with mineral diesel in most modern compression engines. The manufacturing process for biodiesel is similar whatever natural product oil feedstock is used: triglyceride oil extracted from the plant is transesterified into

alkyl esters using a catalyst to yield 3 mol of ester and 1 mol of glycerol per mol of triglyceride used. The glycerol is an unwanted byproduct and must be removed before the biodiesel can be used as a fuel as the viscosity of the glycerol present impedes the high pressure injection system of a modern diesel engine. The major stumbling block to the widespread use of biodiesel is that it is cheaper to drill and refine mineral diesel oil than to grow, extract, transesterify, and purify biodiesel using the conventional methods of adsorption over silica membrane reactors or the addition of lime and phosphoric acid. In order to solve this, several research groups have been working on new methods for extracting glycerol from biodiesel using DESs. The use of DESs in the synthesis of biodiesel have also recently become a subject of a review.²⁴⁷

In 2007, Abbott et al. successfully extracted excess glycerol from biodiesel in the presence of KOH using a Lewis basic mixture with a ratio of salt:2 glycerol using a DES (choline chloride:glycerol, 1:1).²⁴⁸ A 25% portion of the choline chloride was subsequently recovered from the mixture by adding 1-butanol as a liquid cosolvent. A collaboration between the University of Malaya, Malaysia; the King Saud University, Saudi Arabia; and Sultan Qaboos University, Oman has investigated the findings of Abbott et al. confirming that the optimum molar ratio for the choline chloride:glycerol DES is 1:1 and that the most glycerol was extracted using a 1:1 mixture of biodiesel:DES.²⁴⁹ The group also found that two different DESs consisting of choline chloride and the hydrogen bond donor ethylene glycol or 2,2,2-trifluoroacetamide^{250,251} were also successful in extracting glycerol from biodiesel. Recently, they have reported that choline chloride based DESs with ethylene glycol and triethylene as the hydrogen bond donor were successful in removing all free glycerol from palm-oil-based biodiesel,²⁵² although to date no further advances have been reported by this collaboration on recovering the glycerol from the DES. Choline chloride:ethylene glycol and choline chloride:2,2,2-trifluoroacetamide have also been proven to successfully remove glycerol from palm-oil-based biodiesel.²⁵³

The successful recovery of glycerol from biodiesel would, however, pose a new conundrum: Can the recovered glycerol be put to use? Glycerol has some uses as viscosity modifiers and freezing point suppressants; however, with an annual production in excess of 1 million tonnes the market is saturated. Glycerol is poorly combustible so it cannot be used as a fuel and is regarded by many as a waste product. One solution to this problem has been reported by Abbott et al., who have developed a sustainable way of preparing nontoxic tunable DESs with glycerol as the hydrogen bond donor.²⁵⁴ Eutectic mixtures of glycerol with choline chloride were shown to circumvent some of the difficulties associated with using glycerol as a solvent, such as high viscosity and high melting point. The application of these liquids to the esterification of glycerol was used to demonstrate the ability to tune a reaction with the quaternary ammonium acting as a quasiprotecting group. A feature article published by a group from the Universidad de Oviedo, Spain, reviewed attempts to increase the worth of glycerol extracted from biodiesel as an environmentally friendly reaction medium for synthetic organic chemistry.²⁵⁵

In an alternative approach, choline chloride and choline acetate based deep eutectics have been investigated as suitable solvents for lipase activation and enzymatic preparation of biodiesel.²⁵⁶ A 1 choline acetate:1.5 glycerol liquid was found to have low viscosity and good compatibility with Novozym 435, a commercial immobilized *Candida antarctica* lipase B. It was

demonstrated that, in a model biodiesel synthesis system, there were high conversion rates (97%) for the enzymatic transesterification of Miglyol oil 812 catalyzed by the Novozym 435 containing DES. Choline chloride:glycerol has also been used as a solvent for the enzymatic preparation of biodiesel from soybean oil.²⁵⁷ Choline chloride:glycerol has been used as the activator and solvent in the CaO-catalyzed transesterification of rapeseed oil to produce biodiesel.²⁵⁸ DESs have also been utilized to reduce the free fatty acid content of low grade crude palm oil for biodiesel production.²⁵⁹

5. CONCLUSIONS

This review has revealed that interest in DESs has grown significantly in the 10 year period since their first description. The similarity in physical properties between DESs and ILs suggests that they belong in the same class of liquid which is distinct from molecular liquids; yet, the disparity in chemical properties between the liquids means that to date DESs have found very different application fields to ILs. The metal finishing industry is being restricted by legislation, toxicity issues, and cost; DESs offer a viable alternative to existing technologies, and hence, the application and scale-up of these processes have received considerable attention. While research into DESs has mainly focused on their application in metal finishing, DESs are beginning to be used in various synthetic applications; the limited reactions that have been investigated prove the potential of DESs in this area. Thus far, only a narrow range of DESs have been utilized: the future offers significant potential to expand the types of salts and hydrogen bond donors which are used and hence further increase the applications of these solvents.

AUTHOR INFORMATION

Corresponding Author

*E-mail: emma.smith@ntu.ac.uk.

Notes

The authors declare no competing financial interest.

Biographies



Emma L. Smith is a Senior Lecturer in Physical Chemistry at Nottingham Trent University. She received her Ph.D. in Chemistry from Loughborough University. She has been researching electrolytic processes in deep eutectic solvents for the past 7 years. Her research interests have focused on sustainable, functional coatings, concentrating on the electrochemical, physical, and mechanical properties of metallic and polymeric films.



Andrew P. Abbott is Professor of Physical Chemistry at the University of Leicester. He has been at Leicester for 20 years, and his research has focused on the characterization and application of novel solvent media. He started research in the area of ionic liquids in 1997, and this led to the spin out company Scionix Ltd. which aids with the application of deep eutectic solvents. He has published over 130 papers with 70 in the field of ionic liquids and DESs.



Karl S. Ryder is Professor of Physical Chemistry at the University of Leicester and also a Royal Society Industry Fellow with Rolls-Royce plc (Aerospace). He has published over 70 peer reviewed papers as well as coauthored book chapters and has 8 years experience in working with electrolytic processes in ionic liquids and deep eutectic solvents. He has worked on many collaborative projects in scale-up for industrial applications in metal finishing and circuit board technology. Prof. Ryder receives funding from the European Union on a range of projects including energy storage and metal finishing as well as from the U.K. Government and the Royal Society.

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