Electroplating in Deep Eutectic Solvents (DESs)

Research Project

Submitted to the department of chemistry in partial fulfillment of the requirements for the degree of BSc. in chemistry

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May – 2019
ABSTRACT

Deep eutectic solvents (DESs) constitute a class of compounds sharing many similarities with properly named ionic liquids (ILs). The accepted definition of ionic liquid consisting of ions and is a fluid (liquid at T<100 °C), while DESs are eutectic mixtures of Lewis or Brønsted acids and bases made by the action of hydrogen bond formation systems. Their most attractive properties are the wide potential windows and their chemical properties significantly different from aqueous solutions. In the last few decades, the possibility to electrodeposit decorative and functional coatings employing deep eutectic solvents as electrolytes has been widely investigated. A large number of the deposition procedures described in literature, however, large scale application in the industry is somewhat difficult due to competition with existing processes, cost or difficult scalability. From one side, there is the real potential to replace existing plating protocols and to find niche applications for high added-value productions; to the other one, this paves the path towards the electro deposition of metals and alloys thermodynamically impossible to be obtained via usual aqueous solution processes. This project is concerned with demonstrating the answer of what are DESs and why they behave in this manner.
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1. INTRODUCTION

In the last two decades, ever since the potential for new chemical technologies was classical ionic liquids ILs, the research into deep eutectic solvents (DESs) is comparatively in its infancy, with the first paper on the subject only published in 2001. However, with publications from 2001 and in 2012 approaching 200 an increasing amount of research effort is focusing on this emerging field. 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. In this project aims to show what are DESs, what are their properties, how are prepared and what are their applications. (Smith et all. 2014), (Zhang et all.2012), (Abbott et all.2004), (Abdullah and Kadhom.2016), (Tomé et all.2018), (Wang et all.2017).

1.2. Deep Eutectic Solvents

DESs are liquids made from big, non-symmetric ions (shown in Figure 1) that have low lattice energy and later low melting points. They are usually achieved by the completion 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 halide ion and the hydrogen-donor moiety is answerable for the decrease in the melting point of the mixture relative to the melting points of the specific components. (Smith etall. 2014),(Zhang et all.2012), (Abbott et all.2004), (Abdullah and Kadhom.2016), (Tomé et all.2018).
2. TYPES OF DESs

In general, there are four types of DESs

A) Type I : Metal salt + organic salt (e.g. ZnCl$_2$ + Choline chloride)

B) Type II : Metal salt hydrate + organic salt (e.g. CoCl$_2$.6H$_2$O + Choline chloride)

C) Type III : Hydrogen bond donor + organic salt (e.g. urea + Choline chloride)

D) Type IV :(metal halide and hydrogen bond donor)

Type I DESs

The interactions between different metal halides and the halide anion from the quaternary ammonium salt will all produce similar halo metal late species with analogous enthalpies of formation. This suggests that $\Delta T_f$ values should be between 200 and 300 °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 °C or less. It is evident therefore why metal halides such as AlCl$_3$ (MP = 193 °C) FeCl$_3$ (308), SnCl$_2$ (247), ZnCl$_2$ (290) all produce ambient
temperature eutectics. (Smith et all. 2014), (Zhang et all.2012), (Cruz et all.2013), (Tomé et all.2018).

**Type II DESs**

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 consistent anhydrous salt. Clearly the waters of hydration decrease the melting point of metal salts because they decrease the lattice energy. The only system fully described to date is that of CrCl$_3$.6H$_2$O, although others including CaCl$_2$.6H$_2$O, CoCl$_2$.6H$_2$O are described in the patent literature. 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.(Smith et all. 2014), (Zhang et all.2012), (Cruz et all.2013), (Tomé et all.2018).

![Figure (2): 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.](image-url)
Type III DESs

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. In the same study the depression of freezing point was shown to be related to the mass fraction of HBD in the mixture (Smith et all. 2014), (Zhang et all.2012), (Cruz et all.2013), (Tomé et all. 2018)

Type IV DESs

They are formed from metal halide and hydrogen bond donor. (Zhang et all.2012), (Cruz et all.2013), (Tomé et all.2018).

3. PROPERTIES OF DESs

While DESs and conventional ILs have deferent chemical properties, they have analogous physical properties, in particular the potential as tunable solvents that can be modified to a particular type of chemistry; they also exhibit a low vapor pressure, relatively wide liquid-range, and non-flammability. DESs have several advantages over traditional ILs such as their ease of preparation, and easy accessibility from relatively reasonable 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 keeps a moderately low production cost with respect to straight ILs (such as imidazolium based liquids) and licenses large scale applications. (Smith et all. 2014), (Zhang et all. 2012).

3.1. Phase Behavior

The difference in the freezing point at the eutectic composition of a double mixture of A + B compared to that of a theoretical ideal mixture ( ΔTf ), is related to
the amount of the interaction between A and B. The larger the interaction; the larger will be $(\Delta T_f)$. This is shown schematically in Figure 3: Eutectic systems with a very large depression of the melting point in the region of 200 °C are called deep eutectic solvents (DESs). In comparison to ionic liquids (ILs), which consist of a cation and a complex anion or the other way round, DESs comprise a cation, an anion and a completing agent. (Smith et al. 2014), (Zhang et al. 2012), (Abbott et al. 2004).

![Figure 3: Schematic representation of an eutectic point on a two-component phase diagram.](image)

### 3.2. Density

The density is one of the most important physical properties for a solvent. Generally, densities of DESs are determined by means of a specific gravity meter. Table 1 lists the density data of common DESs. Most of DESs exhibit higher densities than water. For instance, type IV ZnCl$_2$–HBD eutectic mixtures have densities higher than 1.3 g cm$^{-3}$. Among them, density of ZnCl$_2$–urea (1 : 3.5) and ZnCl$_2$–acetamide (1 : 4) are different (1.63 and 1.36 g cm$^{-3}$, respectively). This notable difference of density might be attributed to a different molecular organization or packing of the DESs. Note that densities of both DESs are higher than those of pure HDBs (acetamide: 1.16 and urea: 1.32 g cm$^{-3}$). This phenomenon may be explained by the hole theory. Similar to imidazolium-based ILs, DESs are composed of holes or empty vacancies. When ZnCl$_2$ was mixed with urea for
instance, the average hole radius was decreased, resulting in a slight increase of the DESs density as compared to that of neat urea. (Smith et al. 2014), (Zhang et al. 2012), (Durand et al. 2013).

Table (1): Densities of common DESs at 25°C

<table>
<thead>
<tr>
<th>Salt : HBA</th>
<th>Salts HBD (mol : mol)</th>
<th>Density ($p$, g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtNH$_3$Cl</td>
<td>CF$_3$CONH$_2$ 1 : 1.5</td>
<td>1.273</td>
</tr>
<tr>
<td>EtNH$_3$Cl</td>
<td>Acetamide 1 : 1.5</td>
<td>1.041</td>
</tr>
<tr>
<td>EtNH$_3$Cl</td>
<td>Urea 1 : 1.5</td>
<td>1.140</td>
</tr>
<tr>
<td>ChCl</td>
<td>CF$_3$CONH$_2$ 1 : 2</td>
<td>1.342</td>
</tr>
<tr>
<td>AcChCl</td>
<td>Urea 1 : 2</td>
<td>1.206</td>
</tr>
<tr>
<td>ChCl</td>
<td>Urea 1 : 2</td>
<td>1.25</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>Urea 1 : 3.5</td>
<td>1.63</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>Acetamide 1 : 4</td>
<td>1.36</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>EG 1 : 4</td>
<td>1.45</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>Hexanediol 1 : 3</td>
<td>1.38</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol 1 : 2</td>
<td>1.18</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol 1 : 3</td>
<td>1.20</td>
</tr>
</tbody>
</table>

3.3. Viscosity

Like most of the ILs, viscosity of DESs is an important issue that needs to be addressed. Except for ChCl$_2$–ethylene glycol (EG) eutectic mixture, most of the DESs exhibit relatively high viscosities (>100 CP) at room temperature. The high viscosity of DESs is often attributed to the presence of an extensive hydrogen bond network between each component, which results in a lower mobility of free species within the DES. The large ion size and very small void volume of most DESs but also other forces such as electrostatic or van der Waals interactions may contribute to the high viscosity of DES. Owing to their potential applications as green media, the development of DESs with low viscosities is highly desirable. In general, viscosities of eutectic mixtures are mainly affected by the chemical nature of the DES components (type of the ammonium salts and HBDs, organic salt/HBD molar ratio, etc.), the temperature, and the water content. As discussed above, viscosity of DES is also dependent on the free volume. Hence, the hole theory can also be used to design...
DESs with low viscosities. For instance, use of small cations or fluorinated hydrogen-bond donors can lead to the formation of DES with low viscosity. Viscosity of binary eutectic mixtures is essentially governed by hydrogen bonds, van der Waals and electrostatic interactions. Table (2) lists the viscosity data of common DESs at different temperatures. It can be seen that the viscosity of ChCl₂-based DESs is closely dependent on the nature of the HBD. For instance, ChCl₂/EG (1:4) DES exhibits the lowest viscosity (19 CP at 20 °C). In contrast, use of derived sugars (e.g., xylitol, sorbitol) or carboxylic acids (e.g., malonic acid) as HBDs led to DESs exhibiting high viscosities (e.g., 12 730 CP at 20 °C for ChCl₂/sorbitol) due to the presence of a more robust 3D intermolecular hydrogen-bond network. (Smith et al. 2014), (Zhang et al. 2012), (Durand et al. 2013).

Table (2): Viscosities of selected DESs at different temperatures

<table>
<thead>
<tr>
<th>Organic Salt</th>
<th>HBD</th>
<th>molar ratio</th>
<th>Viscosities (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChCl</td>
<td>Urea</td>
<td>1 : 2</td>
<td>750 (25 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Urea</td>
<td>1 : 2</td>
<td>169 (40 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>EG</td>
<td>1 : 2</td>
<td>36 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>EG</td>
<td>1 : 2</td>
<td>37 (25 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>EG</td>
<td>1 : 3</td>
<td>19 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>EG</td>
<td>1 : 4</td>
<td>19 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glucose</td>
<td>1 : 1</td>
<td>34400 (50 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol</td>
<td>1 : 2</td>
<td>376 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol</td>
<td>1 : 2</td>
<td>259 (25 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol</td>
<td>1 : 3</td>
<td>450 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Glycerol</td>
<td>1 : 4</td>
<td>503 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>1,4-Butanediol</td>
<td>1 : 3</td>
<td>140 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>1,4-Butanediol</td>
<td>1 : 4</td>
<td>88 (20 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>CF₂CONH₂</td>
<td>1 : 2</td>
<td>77 (40 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Imidazole</td>
<td>3 : 7</td>
<td>15 (70 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>ZnCl₂</td>
<td>1 : 2</td>
<td>85000 (25 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Xylitol</td>
<td>1 : 1</td>
<td>5230 (30 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Sorbitol</td>
<td>1 : 1</td>
<td>12730 (30 °C)</td>
</tr>
<tr>
<td>ChCl</td>
<td>Malonic acid</td>
<td>1 : 2</td>
<td>1124 (25 °C)</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>Urea</td>
<td>1 : 3.5</td>
<td>11340 (25 °C)</td>
</tr>
<tr>
<td>Bu₄NBr</td>
<td>Imidazole</td>
<td>3 : 7</td>
<td>810 (20 °C)</td>
</tr>
<tr>
<td>EtNH₂Cl</td>
<td>CF₂CONH₂</td>
<td>1 : 1.5</td>
<td>256 (40 °C)</td>
</tr>
</tbody>
</table>

4. PREPARATION OF DESs

From a practical and experimental point of view, DES are generally prepared by mixing hydrogen bond acceptor(HBA) and HBD at an appropriate temperature, the two components are mixed and heated together in closed vessel until
a homogeneous liquid is obtained. Since the original work of Abbott in 2003, where the solid starting materials CHCl₂ and urea were heat data 1:2 molar ratio to obtain a mixture that was liquid at room temperature, many DESs have been prepared, as reviewed in and more details are given in Table (3). For the correct design of DESs, and to rationally expand their applications, a detail understanding and of the physical properties of these solvents is of the utmost importance. (Tang et al. 2015), (Lobo et al. 2012), (Molnar et al. 2017), (Lucia et al. 2017), (Tomé et al. 2018).

<table>
<thead>
<tr>
<th>DESs</th>
<th>Molar ratio</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl / urea</td>
<td>1:2</td>
<td>Direct mixing and stirring of the components at 80°C</td>
</tr>
<tr>
<td>CHCl / oxalic acid</td>
<td>1:1</td>
<td>Direct mixing and stirring of the components at 60°C</td>
</tr>
<tr>
<td>Metal salts / alcohol or amides</td>
<td>Depend on the metal salt</td>
<td>Direct mixing and stirring of the components at 100°C</td>
</tr>
<tr>
<td>CHCl / glycerol</td>
<td>1:2</td>
<td>Direct mixing and stirring of the components at 80°C</td>
</tr>
<tr>
<td>CHCl / ethylene glycol</td>
<td>1:2</td>
<td>Direct mixing and stirring of the component at 80°C</td>
</tr>
<tr>
<td>ZnCl₂ / urea</td>
<td>1:3.5</td>
<td>Direct mixing and stirring of the components at 80°C</td>
</tr>
</tbody>
</table>

5. APPLICATION OF DESs

Having established themselves in the last couple of decades as convenient green alternatives to aqueous and conventional solvents, the potential applications of DES have been widely explored. The major research efforts have been focused in some fields: metal processing, polymer, lubricants and non materials sciences. Here the main applications of DESs in general is presented and more specifically focusing on the application of DESs as base Metal Processing application (Smith et al. 2014), (Ramon et al. 2017).
• Metal Processing Applications such as Metal Electro deposition and Metal Electro polishing
• Synthesis application such as Ion thermal Synthesis, Gas Adsorption, Bio transformations and Transformations of Unprotected Sugars, Cellulose, and Starch
• Application of DESs in polymer science such as solvents, functional additives and as monomers
• As base lubricants

6. ELECTRODE POSITION (ELECTROPLATING)

6.1. Introduction to electrode position

Almost the entire electroplating sector is currently based on aqueous acidic or basic solutions although some specialist applications do use organic solvents, (Graham, A. K., 1995) 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 non soluble 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 completing 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 water course. (Konig, U.; Sessler, B. 2008) 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. 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 W82–84 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. (Smith, E. L. et all: 2013) (Abbott, A. P. et all: 2009) A range of metal reduction processes have been studied in DESs, including Zn, (Abbott, A. P. et all: 2009), (Abbott, A. P et all: 2011), (Abbott, A. P. et all: 2006) Sn, Cu, (Abbott, A. P. et all: 2009), (Popescu, A. M. et all: 2013) Ni, (Abbott, A. P. et all: 2008) Ag, (Abbott, A. P. et all: 2012) Cr, (Abbott, A. P. et all: 2004) Al, (Abood, H. M. A. et all: 2011) Co, (Gomez, E.; Cojocaru, P. et all: 2011) and Sn. 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: Cr, Al, Cu, Ni, and Zn. 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 electro catalysts, electrochemical sensors, air batteries, and fuel cells.

6.1.1. Chrome electroplating

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 electrode position of chromium (see Figure 4) from a dark green, viscous DES formed between choline chloride and the trivalent chrome salt, CrCl₃·6H₂O, has been reported. (Ferreira, E. et all: 2013) 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 micro cracked), 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 LiCl₂ to the ChCl: CrCl₃·6H₂O mixture was found to allow the deposition of crack free, nano crystalline black chromium films which gave good corrosion resistance. (Abbott, A. P.; Capper, G. et all: 2004).
Figure 4. SEM image of a chrome deposit formed following the electrolysis of 1:2 ChCl: CrCl3.6H2O 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.

6.1.2. Aluminum electroplating

The electrode position 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 tri ethyl aluminum 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 AlCl3 based ILs has delayed the progress in their use in many applications since they must be prepared and handled under inert gas atmosphere. (Endres, F. et all: 2006) 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. 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 AlCl3 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, [AlCl2-urea]+ and [AlCl4]−, and it is a suitable medium both for the electrode position of Al metal and the acetylation of ferrocene.
6.1.3. Copper electroplating

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. (Popescu, A.-M. J. et al: 2011). 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 Cu$^+$/Cu$^{2+}$ redox couple using chronoamperometry, cyclic voltammetry, and impedance spectroscopy in ChCl: ethylene glycol. (Lloyd, D. et al: 2011). The reaction was found to be quasar eversible, 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 [CuCl$_3$]$^{2-}$ and that of Cu$^{2+}$ [CuCl$_4$]$^{2-}$.

Pollet et al. have reported the effects of ultrasound at different powers and frequencies on the electrode position of CuCl$_2$ in both aqueous KCl and ChCl: glycerol. (Pollet, B. G. et al: 2008) 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.

6.1.4. Nickel electroplating

Recent studies have demonstrated the electrolytic deposition of nickel from nickel chloride di hydrate dissolved in ChCl: urea and ChCl: ethylene glycol. (Abbott, A. P.; El Ttaib, K. et al: 2008). 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 ethylene di amine (en) and acetyl acetonate (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. (Yang, H. et al: 2011). 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. Thermo chromic 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 NiCl$_2$·6H$_2$O, CrCl$_3$·6H$_2$O, FeCl$_3$, and CoCl$_2$·6H$_2$O in ChCl: ethylene glycol or ChCl: urea. (Gu, C.-D. et al: 2011). It was found that only NiCl$_2$·6H$_2$O exhibited significant, stable, thermo chromic behavior over a wide temperature range. The color of 0.1 M NiCl$_2$6H$_2$O dissolved in DES changed from pale green (room temperature), to spring green (∼70 °C), to blue (∼120 °C). Incorporating the Ni containing DES into a micro porous PVDF film produced a thermo chromic PVDF composite film for application in high performance thermo chromic materials. The same authors published some interesting work using DESs to fabricate nanostructured Ni metal films (Gu, C.; Tu, J. Langmuir :2011) using constant voltage, pulse voltage, and reverse pulse voltage. A variety of nanostructured Ni films were produced with micro / Nano binary surface architectures such as Nano sheets, aligned Nano strips, and hierarchical flowers (see Figure 5). Electrochemical measurements revealed that the super hydrophobic Ni films exhibited an obvious passivation phenomenon, which may provide enhanced corrosion resistance in aqueous solutions.
6.1.5. Zinc electroplating

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 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. 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. The double layer effects on zinc nucleation have been studied by Ryder et al. (Abbott, A. P. et al: 2011). Zn electrode position 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: [ZnCl4] 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 6).

Figure 6. Tapping mode, liquid AFM images recorded in a 0.3 M ZnCl₂ 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 = 600s.

7. CONCLUSIONS

In this project it could be concluded that the interest in DESs has grown significantly in the last two decades since 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.
8. REFERENCES


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