



Challenges to the Adoption of Deep Eutectic Solvents in the Electrodeposition Industries

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In the past 20 years there has been a considerable interest in the application of deep eutectic solvents (DESs) for metal finishing applications and a large number of academic studies have been performed related to electrodeposition, electroless deposition and electropolishing. These DES materials possess a number of unique characteristics and it was predicted that they would replace hazardous and toxic materials associated with many aqueous-based processes and make them inherently greener and more sustainable. They would also facilitate the deposition of metals and alloys that are difficult or impossible to deposit from aqueous solutions. However, until now there have only been limited demonstrations of scaled-up processes, and their commercialisation and deployment in the metal finishing industries has not eventuated. In this paper we reflect on some of the reasons why and identify some key limitations of DES-based surface finishing processes. Unless these barriers can be overcome, it will be difficult for DESs to be adopted in these industries.

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Deep eutectic solvents (DESs) are a class of green solvents with unique and tuneable properties and since their initial discovery^{1,2} in 2003–2004 many prospective applications have been identified.³ DES materials are sometimes considered a sub-class of ionic liquids (ILs) but, as well as comprising of ionic species, they also contain neutral molecules and, due to their hygroscopicity, trace amounts of water. They share some of the important characteristics of conventional ILs such as low volatility, high conductivity, non-flammability, good recyclability and high thermal stability.^{3,4} Additionally, they have some advantages over ILs in that they are much cheaper, are easier to prepare and handle, and have superior green credentials in terms of toxicity, sustainability and biodegradability.^{3,4} Potentially a very large number of DES materials can be synthesised and they have considerable potential as green “designer” solvents with tuneable physico-chemical properties.

The definition of what constitutes a deep eutectic solvent is somewhat contentious and the meaning has evolved somewhat since the original discovery.² However, the most commonly accepted definition is that they are a mixture of Lewis and Brønsted acids and bases which have a lower freezing point than either of the components.⁵ This is often low enough (<100 °C) for them to function as novel solvents and electrolytes. Originally the term referred to a eutectic mixture of a quaternary ammonium salt (QAS) with various carboxylic acids,² but this has now broadened to include many other systems (see Table I).^{3–5} A DES is typically formulated by complexing the QAS (a hydrogen bond acceptor, HBA) with a hydrogen bond donor (HBD) and it is believed that hydrogen bonding between these components and the resulting charge delocalisation is largely responsible for the observed lowering of the freezing point of the eutectic mixture.⁵

Type I DESs are defined as consisting of mixtures of QAS and a metal halide salt, and are analogous to existing ionic liquids formulated from imidazolium salts. Type II DESs are formulated from a QAS and a hydrated metal salt and this expands the number of systems that can be explored and reduces their sensitivity to moisture. However, the most common DES materials are type III which consist of eutectic mixtures of a QAS (e.g. choline chloride) as the acceptor, and a hydrogen bond donor (HBD) which are typically carboxylic acids, alcohols or amides. Some common examples of type III eutectics are shown in Fig. 1 and their key properties are summarised in Table II. Type IV and V DESs are also known but are rarely employed in metal finishing studies.

The desirable properties of DESs has led to many prospective applications in areas such as metal finishing, extractive metallurgy, separation and gas capture, battery technologies, organic synthesis and catalysis, biomass processing, pharmaceutical research and synthesis of nanomaterials. The technical literature on DESs both on the fundamental and applied side is vast and some idea of its scope can be found in a number of recent review articles.^{4,6,7} The first applications for DESs related to electrochemistry as these materials have a wide electrochemical window and possess relatively good ionic conductivity.^{3,8,9} The majority of these studies have focussed on electrodeposition, but electropolishing, electroless processes and etching have also been explored.^{10–13} Of particular interest was the possible use of DESs to electrodeposit metals (e.g. Al, Mg, Ti, W, Cr) which are difficult or impossible to deposit from aqueous electrolytes. Although this can be achieved with standard ILs, their prohibitive costs make DES-based processes more attractive.

The literature on metal finishing employing DESs is again large and more than 500 research articles and reviews have been published in the time period 2004–2024. Figure 2 indicates that the number of publications per year grew steadily until 2020 but has been relatively constant since then at 50–60 publications per year. The vast majority of the papers are on electrodeposition (89%) although there are significant numbers of papers on electropolishing (8%) and electroless/immersion processes (3%). For the former category, Figs. 3 and 4 summarise the various metals and binary alloys that have been electrodeposited from DESs over that period. In addition to these, ternary alloys, composites and semiconductor materials have also been prepared from DESs. There are many useful review articles^{8–15} and monographs^{16,17} which summarise the main research activities undertaken between 2004 and 2024 related to DES and IL materials.

The majority of these publications related to lab-scale electrochemical studies of the DES system using cyclic voltammetry, impedance, hydrodynamic and EQCM techniques under potentiostatic control in a conventional three-electrode configuration.¹⁷ Studies of nucleation phenomena and the very early stages of film growth are also very common. These fundamental studies are important but often have less relevance to actual electroplating processes which involve depositing relatively thick metal films (0.1–20 μm) under galvanostatic conditions. Typically, in industrial plating, emergent characteristics such as throwing power, current efficiency, deposition rate, deposit properties (e.g. hardness, stress, alloy composition, roughness and microstructure) and process control issues are of more concern than developing detailed mechanistic or atomistic models of deposition.

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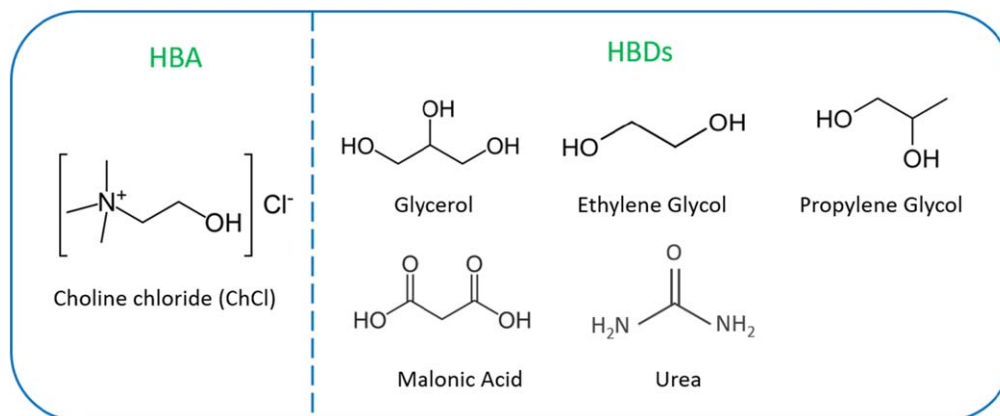


Figure 1. Hydrogen bond acceptor (HBA) and various hydrogen bond donors (HBDs) used for formulating type III deep eutectic solvents in metal finishing studies.

Table I. The classification of some common types of deep eutectic solvents.

DES type	Acceptor species	Donor species
Type I	QAS	Metal halide
Type II	QAS	Hydrated metal halide
Type III	QAS	Hydrogen bond donor (HBD)
Type IV	Hydrated metal halide	Hydrogen bond donor (HBD)
Type V	HBA	HBD

The initial success of lab-based studies of electrodeposition from DESs naturally led to the possibility that they could be scaled into actual metal finishing processes, in many cases replacing problematic aqueous processes.^{9–13} However, despite the large number of publications in this field, there has been little evidence of them being adopted in the metal finishing industries. In a number of review articles^{10,13,16} published around 2010 it was suggested that these DES processes would be deployed fairly soon (i.e. within a decade) and there were some examples of scaled-up demonstrator and pilot plants. However, 15 years later there is no real evidence of these technologies being deployed in industry.

This lack of industrial adoption mirrors that experienced with the use of DESs and ILs in extractive metallurgy, a field which is often referred to as ionometallurgy¹⁸ or solvometallurgy.¹⁹ Despite some early promise, the field of ionometallurgy has not really developed outside of the lab, and there have been no commercial breakthroughs. In 2023 Binnemans and Jones²⁰ published an insightful article which reflected on the eight key reasons why ILs and DESs

have had negligible impact on the metallurgical industries, and many of these issues apply equally well to the field of metal finishing. While the benefits of DESs for metal finishing are well documented, their deficiencies and limitations are hardly ever mentioned, and there are only a handful of publications^{21–23} which have expressed any scepticism. Barriers to the adoption of ILs in metal finishing have also been briefly discussed^{24,25} and these also have some relevance to DESs. Collectively, these dissenting opinions provide a useful starting point for rationalising why DESs are not being considered for implementation in metal finishing.

Given this background, and based upon our own experiences working in this area from 2006–2020, the present study attempts to identify and critically reflect on the barriers to the adoption of deep eutectic solvents in the metal finishing industries. A central question to address is whether some of these barriers can be negotiated with further research and development or are they essentially insurmountable, making the commercialisation of DES-based processes unlikely. Our initial analysis indicated that there are a number of major barriers of varying severity, and in the following sections these are discussed in detail. The emphasis is on DESs as they are more likely to be industrially useful than ILs, but many of the points raised apply equally to both classes of materials.

Main Barriers to Adoption—Physicochemical and Green Aspects

An initial identification of the limitations of deep eutectic solvents can be conveniently performed by analysing their fundamental physicochemical properties and also issues related to their sustainability, toxicity and greenness. These issues are identifiable at the laboratory-scale and in the early stages of R&D.

Table II. Basic physical properties of some common type III deep eutectic solvents formulated from choline chloride (ChCl) and various hydrogen bond donors. Vapour pressure measured at 100 °C, all other properties measured at 25 °C. Data taken from Refs. 3, 7 and 59.

Property	Ethaline	Reline	Maline	Glyceline
HBA	ChCl	ChCl	ChCl	ChCl
HBD	ethylene glycol	urea	malonic acid	glycerol
Molar ratio (HBA:HBD)	1:2	1:2	1:2	1:2
Density, ρ / g cm ⁻³	1.12	1.24	1.23	1.18
Viscosity, η / cP	36	632	721	376
Surface tension, γ / mN m ⁻¹	49	52	65.7	55.8
Conductivity, κ / mS cm ⁻¹	7.61	0.75	0.55	1.05
Freezing point, T_f / °C	-36	12	10	17
Onset temperature, T_{on} / °C	90	173	128	175
pH	4.4	10.1	1.6	4.5
Vapour pressure / Pa	-	1.3	-	11.6

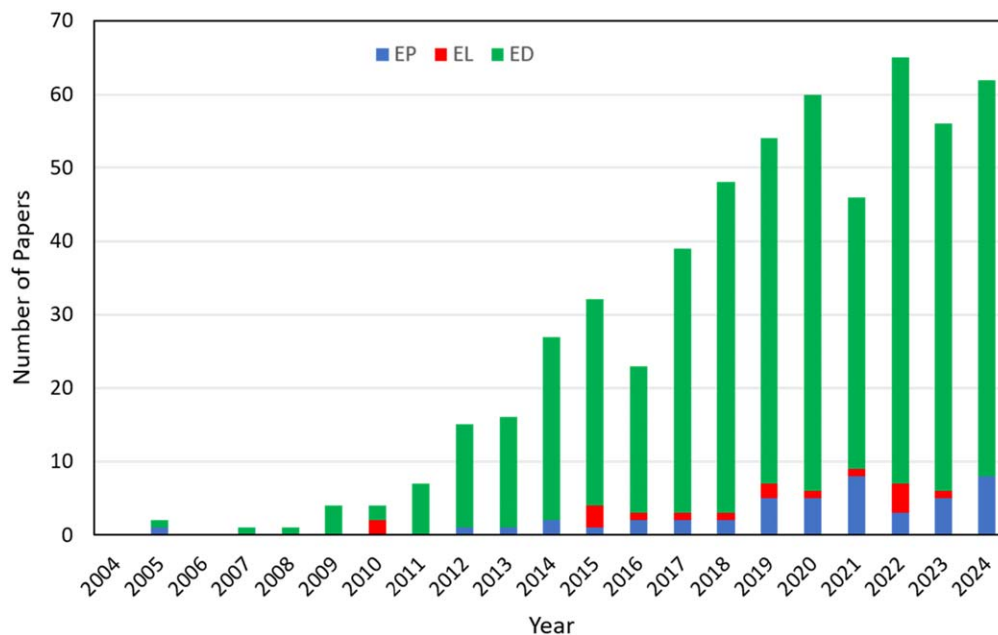


Figure 2. Number of papers published per year involving deep eutectic solvents and various metal finishing processes. ED = electrodeposition/electroplating, EL = electroless/immersion processes and EP = electropolishing. Based on a Scopus analysis with manual screening of sources for relevance.

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Figure 3. Summary of the elements that have been electrodeposited from deep eutectic solvents. Vertical blue lines indicate a metal deposited by electrodeposition as well as an electroless or immersion process; solid blue fill indicates electrodeposition only. A red dot indicates an attempt to scale up the process.

Disputed green credentials and regulatory issues.—Historically DESs have been considered “green” solvents and they are typically described as being sustainable, non-toxic and biodegradable materials.^{4,6} In metal finishing it was envisaged that these materials would replace hazardous and toxic materials (e.g. strong acids and alkalis, cyanide, hexavalent chromium) and make these processes inherently greener.^{8–12} More recently, this narrative has been questioned³ and it has been suggested²⁶ that the “greenness” of DESs appears to be based more on perceptions than actual data. For example, in terms of sustainability, it has been noted that the precursors to many DESs (e.g. choline chloride, ethylene glycol and

urea) are produced at large scale via traditional synthetic routes which typically have poor sustainability.²⁶ The actual production of DESs (involving simple mixing and heating) is more sustainable and a recent life-cycle assessment (LCA) confirms that the synthesis of precursors is the main issue.²⁷

While it is generally true that many DES components can be considered non-hazardous and non-toxic there has been minimal toxicological testing and the available results are incomplete and sometimes contradictory.^{26,28} The toxicity depends on the type of DES and in some cases was higher than for the components alone. Moreover, even if some DESs are inherently non-toxic it has been

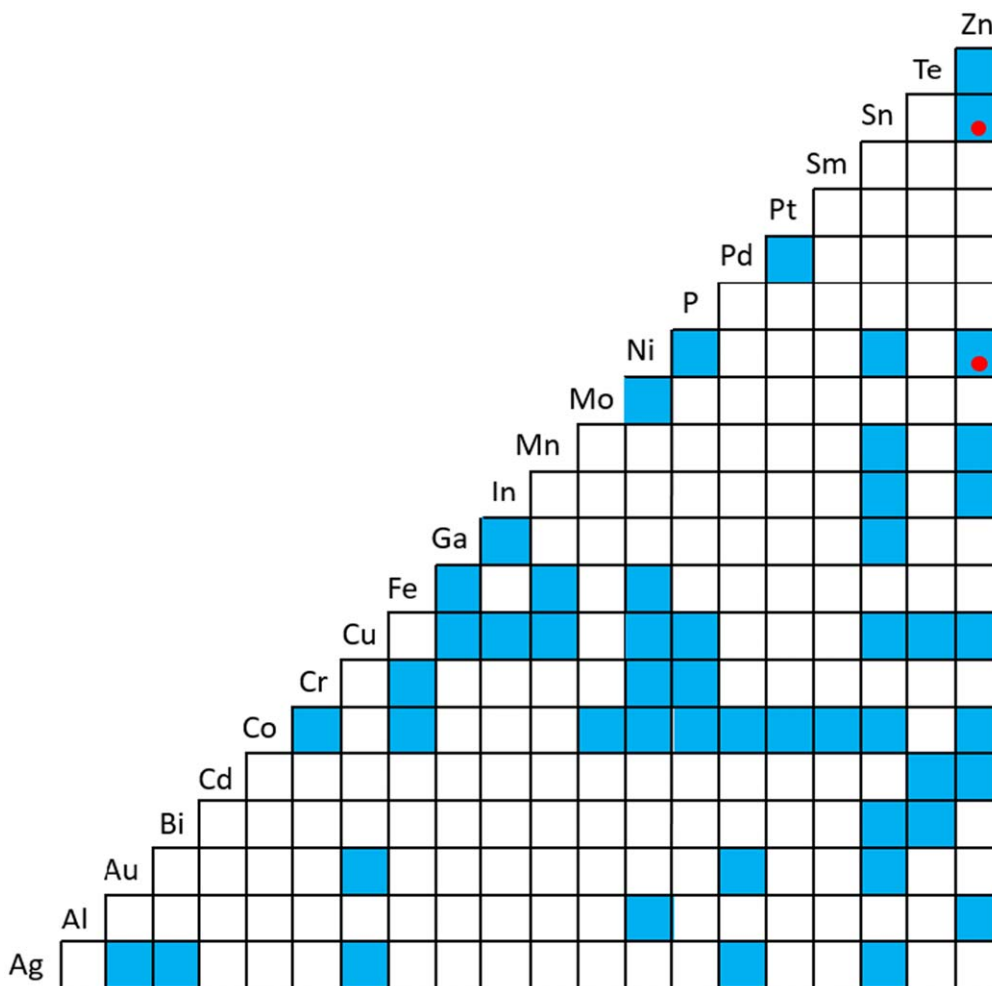


Figure 4. Summary of binary alloys that have been deposited from deep eutectic solvents. A red dot indicates an attempt to scale up the process.

demonstrated that, under certain conditions, they can be thermally²⁹ or electrochemically²¹ decomposed into toxic by-products. Claims that DESs are biodegradable are more justified and closed bottle testing of all common DES formulations indicates that they can all be classified as “readily biodegradable.”²⁸ Importantly, the greenness of DESs cannot be generalised and has to be evaluated on an individual basis. In terms of ranking the greenness of DESs, a recent survey²⁸ concluded that: glyceline > reline > ethaline, but from the metal finishing literature ethaline is perhaps the most useful (and popular) material.

Related to these issues is the necessity for DES materials to satisfy environmental and safety regulations regarding their use. In the European Union the need to register new chemicals under the REACH regulations is particularly onerous, and represents a significant barrier to the introduction of new chemical compounds and processes.²⁵ The constituents of common DESs (e.g. choline chloride, urea, ethylene glycol and glycerol) are all REACH registered, and typically mixtures of REACH-compliant compounds do not have to be registered separately. However, as noted by Binnemans,²⁰ registration under REACH not only applies to the chemicals themselves, but also to the application, so that their use in a new metal finishing process would still require registration. Other countries have similar regulations, and it was reported¹² that ethylene glycol used to formulate some DESs is restricted in certain countries. Propylene glycol is less toxic and can be substituted for ethylene glycol, but with some loss in performance, and is considerably more expensive.³⁰

Given such concerns, replacing well understood and proven aqueous-based processes with DES or IL materials solely on the

basis of eco-friendly or green credentials appears optimistic. This is especially true when there are additional issues to consider such as cost, energy requirements, materials compatibility, recyclability and when there is little evidence that these novel solvents perform better than existing ones.

High viscosity.—Deep eutectic solvents typically have viscosities, η , that are 10–100 higher than aqueous solutions and have fluidities similar to thick oils (Table II).^{3,4,7} Even the least viscous DES (ethaline) has a viscosity of $\eta = 36$ cP at 25 °C and for the other common DES materials such as reline ($\eta = 632$ cP) it is even higher. These values can be compared to water ($\eta = 0.9$ cP) and 20 wt% sulfuric acid ($\eta = 1.37$ cP) at the same temperature. Viscosity is important as it largely determines the electrical conductivity and transport properties of species in the DES. A high viscosity will result in a low electrical conductivity and low diffusivity of electroactive species and, as will be discussed in detail later, these result in a low electrodeposition rate and poor throwing power. The viscosity can be improved by operating at high temperatures^{2,7,8} or by water additions^{31–33} but these present some additional complications.

The high viscosity of the DES materials makes them problematic to handle in many metal finishing operations. For example, transporting and agitating viscous fluids is more difficult and will consume more energy, and pumps and mixers/eductors will have to be over-sized relative to those used in aqueous systems.^{20,34} The high viscosity also increases metal ion drag-out losses and these have been estimated to be three times higher than for water-based processes, and more rinse water is generated.³⁵ It has been

suggested¹⁷ that these issues can be circumvented by using an air knife to physically remove DES adhered to substrate, or rinsing with liquids that are immiscible with the DES and separating them later, but these approaches have not been demonstrated at scale.

High viscosities can have some advantages, for example, in the electrodeposition of composite materials where colloidal and sedimentation stability is enhanced compared to aqueous solutions.³⁶ Similarly, in electropolishing applications the viscosity of ethaline is comparable to that of strong acids and poses no particular disadvantage.^{37–39} But generally, the high viscosity of DES materials is a serious impediment to their use in metal finishing processes.

Low deposition rates.—One of the main issues with electrodeposition from deep eutectic solvents is the relatively low deposition rates. Most industrial aqueous plating processes⁴⁰ occur at current densities between 5 and 100 mA cm⁻², but a survey of the DES literature indicates typical rates of 0.5–10 mA cm⁻² - an order of magnitude lower. The reasons for this mainly relate to the low diffusivity of electroactive species in the solvents, a direct consequence of the DES materials having very high viscosities. For example, in Table III, a comparison is made of the diffusion coefficient, D , of various metal chloro-complexes in DESs^{22,33,41–44} and their values in the corresponding aqueous system.^{45–48} This data indicates that diffusivities in aqueous solutions are typically 10–50 times higher than for DESs.

The maximum rate of deposition is established by the limiting current, i_{LIM} , which can be calculated as:

$$i_{LIM} = \frac{nFDc}{\delta} \quad [1]$$

where n is the number of electrons transferred in the cathodic process, δ is the diffusion layer thickness, and D and c are the diffusion coefficient and bulk concentration of the electroactive species.⁴⁹ Typically, deposition will be performed at a current density of 20%–80% of i_{LIM} , as exceeding it will lead to deposits with poor morphology. Equation 1 indicates that for similar metal ion concentrations and hydrodynamic conditions (same δ) the limiting current in DES system will always be lower, and this is the underlying reason for the low deposition rates reported in the literature.

Some improvement in D and i_{LIM} values can be achieved by increasing the temperature. In ethaline the activation energy for the diffusive transport of species is typically $E_a \approx 26$ – 30 kJ mol⁻¹.²² Assuming an average value of $E_a = 28$ kJ mol⁻¹ there would be a two-fold improvement going from 25 °C to 45 °C¹ and five-fold enhancement at 75 °C, but the energy requirements are increased. There is little to be gained by increasing the metal salt concentration as their solubility in DES systems is not significantly greater than for

aqueous systems. One recent study⁵⁰ showed that by using a high concentration nickel salt (1.14 M) in ethaline and operating at 90 °C, good Ni deposit properties could be obtained at a current density 15 mA cm⁻². However, this is still at the lower end of what is achievable in an aqueous Watts bath (20–100 mA cm⁻²)⁵¹ and is close to the thermal decomposition temperature of the DES (Table II). Transport can be improved by reducing δ but this is problematic using standard methods due to the high DES viscosity. Ultrasonic agitation has been shown to significantly increase the i_{LIM} in DES in lab-scale experiments but is difficult to implement in a production environment.⁵²

Poor throwing power.—A serious limitation to the use of deep eutectic solvents in electrodeposition relates to their relatively poor throwing power—i.e. the ability to achieve uniform deposit thickness over the substrate/part. The throwing power reflects the prevailing current distribution, and is best quantified in terms of the dimensionless Wagner number, W_a , which defines the ratio of the ohmic resistance to the polarisation resistance. At high polarisation (Tafel region), the Wagner number can be defined by:

$$W_a = \frac{RT\kappa}{\alpha_c Fi_{avg}L} \quad [2]$$

where i_{avg} is the average current density, L is the characteristic length, κ is the solution conductivity, α_c is the cathodic transfer coefficient and RT/F has its usual meaning.⁴⁹ A primary current distribution ($W_a = 0$) is the least uniform, while a secondary current distribution ($W_a > 0$) will tend to improve thickness uniformity. Equation 2 indicates that this latter condition can be achieved with a low value of α_c (i.e. a high Tafel slope), a high value of κ , and a low i_{avg} .

A recent study³³ of copper deposition from DES (ethaline) and an aqueous system at an RDE electrode under comparable conditions yielded $W_a < 0.1$ for the DES and $W_a = 2.0$ for the aqueous system. Figures 5 and 6 illustrates the large differences in the uniformity of the current distribution and deposit thickness for the two systems at the RDE. Note that in this study the characteristic length, L , corresponds to the disc radius, $r_0 = 0.6$ cm. A similar study⁵³ of nickel deposition from a reline-based DES yielded a $W_a \approx 0.02$ while a comparable experiment from an aqueous Watts bath resulted in $W_a = 0.75$. The low values for W_a indicate a near primary (i.e. non-uniform) current distribution exists in these DES systems.

Given that $W_a \propto \kappa/\alpha_c i_{avg}$, and noting that α_c values are similar in aqueous and DES systems, a secondary current distribution can be most readily achieved by increasing conductivity or reducing i_{avg} . The low ionic conductivity of DESs is the main reason why the current distribution tends to be primary—typically this can be 10–10² lower than aqueous systems.^{3,7–9,40,50} This non-uniformity is somewhat offset by i_{avg} tending to be much lower in DES systems, but even under these conditions the current distribution is still close to primary. From a process point of view, this makes it difficult to attain a specification for thickness or alloy composition for complex parts, and will also increase material wastage.

Some of the issues with low conductivity can be mitigated, but only partially. For example, the use of elevated temperatures improves the conductivity (for κ , $E_a \approx 27$ – 28 kJ mol⁻¹ in ethaline²²) so that a fivefold increase could be obtained by operating at 75 °C. Additionally, some alloy deposition from DESs has been performed using barrel plating where the effects of a poor current distribution are minimised to some extent.⁵⁴ However, this approach is not relevant to other configurations such as rack plating. While the use of current thieves and shields may also improve uniformity, they increase the complexity of the plating equipment and require careful optimisation using modelling tools.⁵⁵

The issues related to throwing power reflect those previously encountered for electrodeposition from room temperature ILs, which also possess low conductivity. Figure 7 shows a comparison of the

Table III. A comparison of the diffusivity of various metal chloro-complexes in deep eutectic solvents and in aqueous media.

Species	Electrolyte	Temp (°C)	D (cm ² s ⁻¹)	References
[AgCl ₃] ²⁻	ChCl: urea (1:2)	50	1.3×10^{-7}	41
	3 M NaCl		6.3×10^{-6}	45
[PdCl ₄] ²⁻	ChCl: urea (1:2)	50	1.7×10^{-7}	42
	ChCl: EG (1:2)	50	1.9×10^{-8}	42
	1 M KCl	25	1.1×10^{-5}	46
[FeCl ₄] ⁻	ChCl: EG (1:2)	50	1.7×10^{-7}	22
	0.1 M FeCl ₃		4.8×10^{-6}	47
[CuCl ₄] ²⁻	ChCl: EG (1:2)	25	1.2×10^{-7}	43
	ChCl: urea (1:2)	50	6.8×10^{-8}	44
	1.5 M NaCl	25	4.3×10^{-6}	48

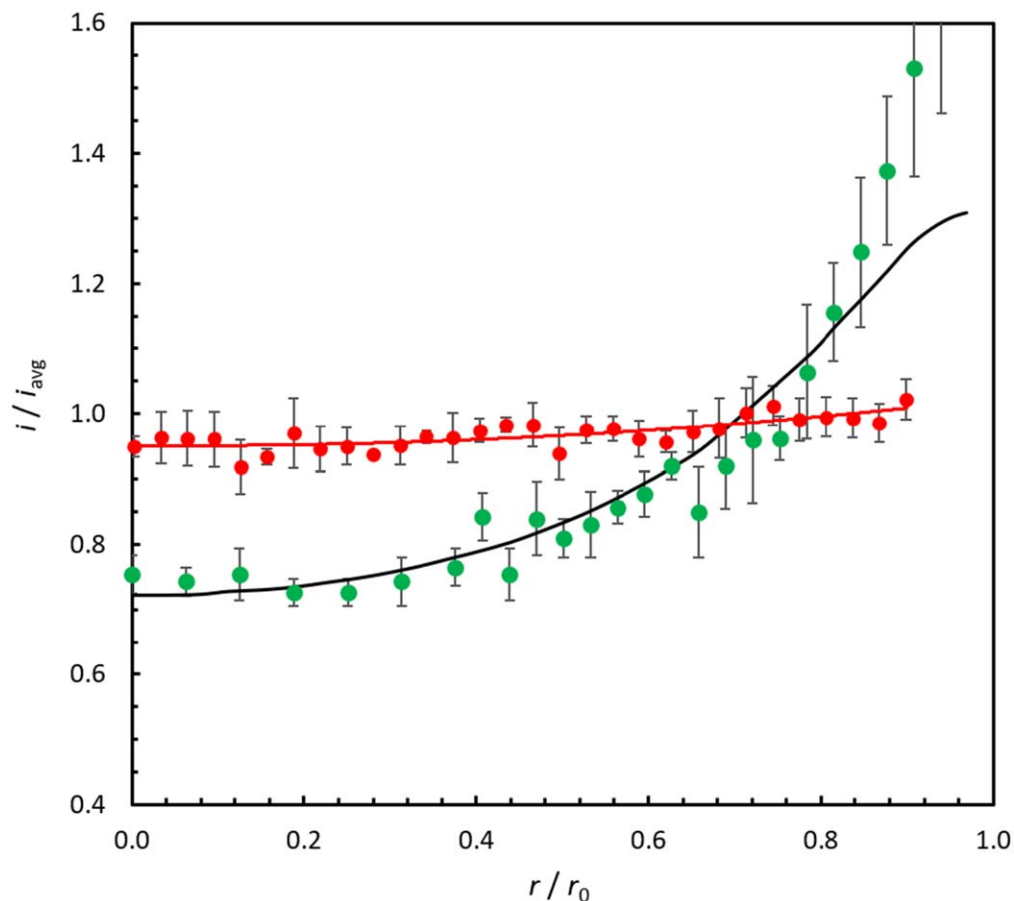


Figure 5. Measured current (thickness) distribution for copper deposition from: (●) 0.20 M Cu_2SO_4 aqueous sample ($W_a = 2.0$) and (●) for 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in an ethaline DES ($W_a = 0.1$) with 6 wt% H_2O . The black line corresponds to the primary current distribution ($W_a = 0$). Samples were deposited at an RDE (radius, r_0) at 80% of their respective limiting currents.

conductivities of various aqueous, organic, IL and DES systems. For additional context, most aqueous metal plating processes operate in the range of 50–600 mS cm^{-1} .⁵⁶ As noted by Hussey⁵⁷ in 2014, “Second generation ILs do not exhibit sufficient conductivity to support the current densities/plating rates needed for viable industrial processes...” and this comment applies equally to DESs. Notably, the Sigal process for the deposition of Al from triethyl aluminium dissolved in toluene operated at a current density of 20 mA cm^{-2} at 100 °C with $\kappa = 250 \text{ mS cm}^{-1}$ and the throwing power was comparable to that of aqueous plating processes.⁵⁸ This process was ultimately uneconomic and had significant safety and environmental issues, but the high deposition rate and good thickness uniformity attained facilitated its adoption as an industrial metal finishing process.

Limited chemical and thermal stability.—DES materials are often considered to possess high chemical and thermal stability and can be employed in relatively high temperature processes (> 150 °C).⁸ However, thermogravimetric (TG) analysis indicates that ethaline can partially decompose with an onset temperature as low as $T_{\text{on}} = 90 \text{ °C}$ while reline is more stable with $T_{\text{on}} = 170 \text{ °C}$.^{59,60} It has been demonstrated that TG onset temperatures overestimate thermal stability and when experiments were performed isothermally for longer durations significant mass losses were observed for ethaline at temperatures as low as 70 °C.⁵⁹ Other studies have shown the formation of toxic decomposition by-products when certain DES are heated to 120–180 °C.^{29,61} The limited thermal stability of DESs suggests that the strategy of increasing temperature to improve fluidity, conductivity and transport properties of the DES has strict limits and cannot be increased

indefinitely. As another instructive example, DESs based on mixtures of choline chloride and carboxylic acids (e.g. malonic acid) are not chemically stable as the alcohol group of the choline reacts with carboxylic acid to form esters.⁶² Once again, claims of high stability for DESs have to be examined on an individual basis and with due consideration of the likely process conditions.

Complex speciation.—Another issue related to DESs is their relatively complex speciation and solution chemistry. While nominally simple eutectic mixtures, their high chloride concentration means that a wide range of metal-chloro-complexes are formed.^{63,64} The existence of such complexes dominates the overall electrochemical characteristics, for example, by shifting the formal potentials to more negative values relative to the uncomplexed ions and stabilising intermediate oxidation states.⁶⁵ The similarity in speciation and electrochemical characteristics of many metal DES systems compared to equivalent “high-chloride” aqueous and IL systems is striking.²³ This is demonstrated in Fig. 8 which shows a comparison of the electrochemical behaviour of Cu in ethaline and an aqueous chloride system.⁶⁶ This figure also illustrates the low current densities attainable in ethaline compared to the aqueous electrolytes due to the low diffusivity of electroactive species.

The metal speciation in various DESs has been extensively studied using spectroscopic techniques including EXAFS, UV-vis, FAB-MS and NMR.^{63,64} For monovalent cations, M^+Cl_2^- and $\text{M}^+\text{Cl}_3^{2-}$ chloro-complexes are mainly formed; and for divalent species it is predominantly $\text{M}^{II}\text{Cl}_4^{2-}$ complexes. In some cases where ethylene glycol (EG) is a DES component, it can also act as a ligand leading to the formation of species such as $[\text{Ni}^{II}(\text{EG})_3]^{2+}$ or mixed complexes such as $[\text{Fe}^{II}(\text{EG})\text{Cl}_2]^{2+}$ and $[\text{Cr}^{III}(\text{EG})\text{Cl}_3]$.^{50,67,68}

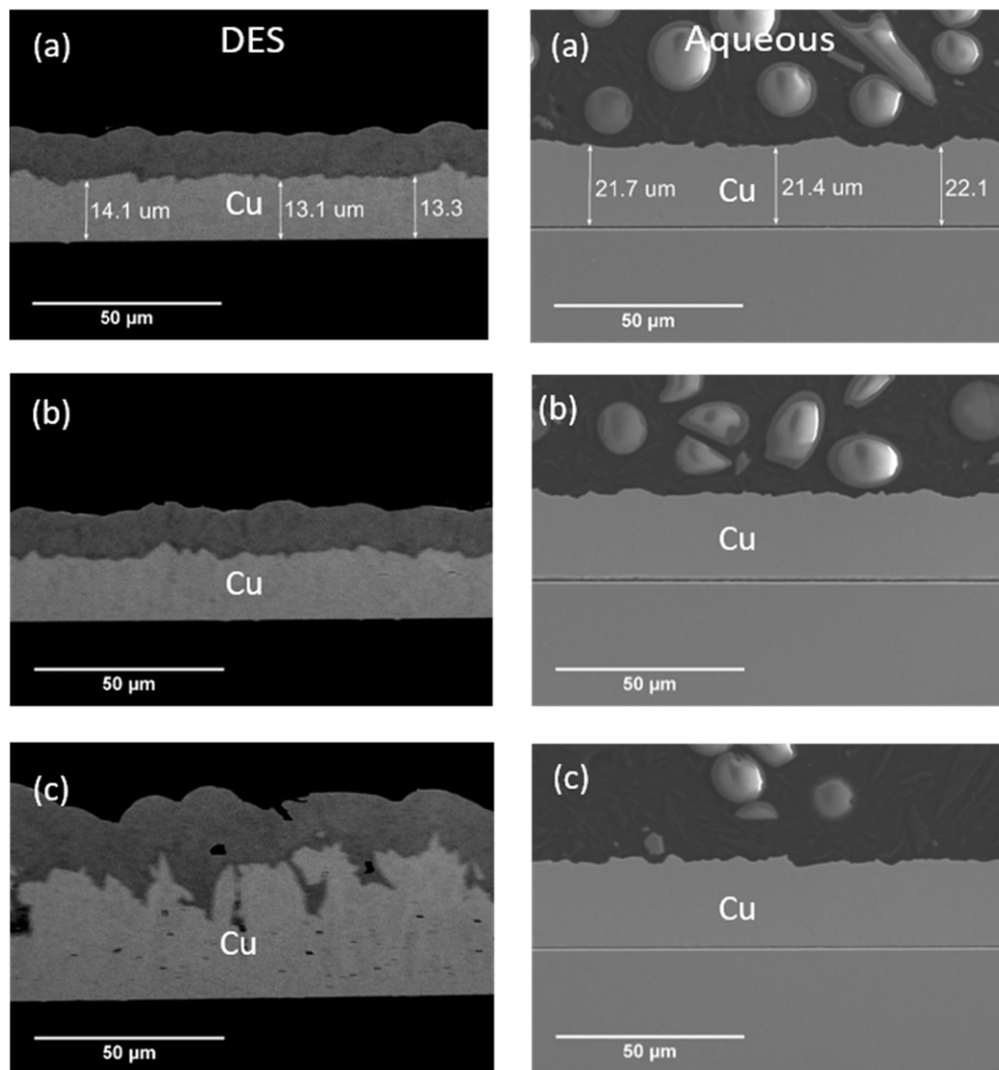


Figure 6. Cross-sectional SEM images of copper deposited from aqueous and DES electrolytes showing the radial variation in deposit thickness: (a) near disk centre $r/r_0 = 0.06$, (b) mid-point $r/r_0 = 0.5$ and (c) near edge $r/r_0 = 0.87$. Note that for the DES samples, the copper was over-plated with Ni to aid edge definition, and at the disk edge the limiting current is exceeded and the deposit is dendritic.

The distribution of the various complexes depends on the molar ratio of the DES components and also on temperature.

Although the metal ion speciation in DES systems has been determined for some conditions, stability constant data are not available so that it is not possible to calculate the species distribution under other conditions. This is in contrast to aqueous plating baths where these constants are known for many commonly used metal-ligand combinations, and these can also be used to calculate the formal potential of the complexes.⁶⁹ Therefore, even though many aqueous plating processes have equally complex speciation, the species distribution can be calculated and used to rationalise experimental results⁷⁰—something that is not yet possible with DESs.

The use of other quaternary ammonium salts with weakly complexing anions (e.g. nitrate, sulfate) might resolve some of these issues, but it is unclear if these would act as suitable hydrogen bond acceptors to allow the formulation of useful DESs.¹ Notably, an attempt to deposit copper from a DES formulated with a non-halide salt (choline citrate) was hampered by relatively high viscosity and low conductivity compared to conventional ethaline.⁷¹ Some simplifications could arise if DES systems did not require additives (brighteners, grain refiners and levellers) but the literature^{72,73} indicates that, as for aqueous systems, these are needed to obtain good deposit properties. Therefore, in addition to the speciation complexities, the monitoring and control of additives will also be needed.

Lack of key property data.—In addition to the above-mentioned issues, there is a lack of accessible data on the physicochemical and material properties of DESs materials that are required to model and scale-up metal finishing processes. Basic properties such as density, viscosity, refractive index, vapour pressure and surface tension have been determined for many DESs, but there is considerable variability in the results due to issues such as purity and water content.^{3,4,6,7} There is more limited data on transport properties (e.g. diffusivity of species) and kinetic data for electrodeposition reactions (Tafel slopes, i_0 and α) is also sparse, even though this information is critical in determining the overall process characteristics. Notably there are some difficulties in obtaining this kinetic data reliably due to issues with high viscosities, low conductivities and the choice of a suitable reference electrode.^{9,23,74,75}

There is also a basic lack of thermodynamic data for DES systems. While there have been attempts to measure formal potentials, E^0 , for some electrode process (e.g. Cu and Ag) this has not been extended to other systems.⁷⁶ Approximate E^0 values have also been estimated using the concept of “on-set potentials,” but this can only be applied to electrochemically reversible systems.⁶⁵ Similarly, there are no values for equilibrium constants (e.g. those reflecting the formation of complexes or related to solubility or dissociation equilibria) that would be required to fully understand and rationalise the solution chemistry and speciation in the DES electrolytes.²¹

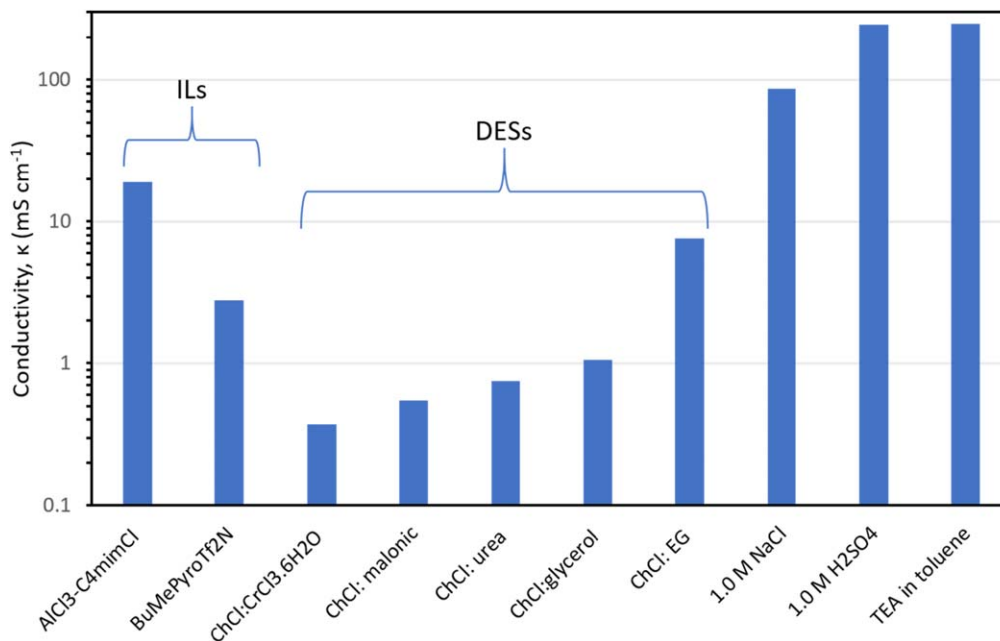


Figure 7. Specific conductivity of various ILs and DESs compared to aqueous and organic electrolytes. Note the log scale. Values of κ measured at 25 °C except for TEA/toluene which is at 100 °C. Data taken from Refs. 3, 17, 57, 58 and 86.

These limitations are in contrast to aqueous systems where there is a wide range of reliable thermodynamic, kinetic and transport data for many species relevant to metal finishing processes. This array of data allows processes to be rationalised and optimised, facilitates modelling and simulation approaches, and allows the construction of Pourbaix and speciation diagrams. Although it must be admitted that historically electroplating process development often proceeded empirically, the lack of data in the DES systems must be considered a serious impediment to its development and wide-spread use.

Hygroscopicity.—Most DES formulations are hygroscopic and without any special precautions (i.e. an inert atmosphere) they will accumulate a few wt% H₂O after being in contact with the open air (Fig. 9).^{32,77,78} This is arguably not a serious problem as, unlike most ILs, they are highly tolerant to water contamination. Notably, in some cases water addition can improve the conductivity³² and transport properties³³ of the DES (Fig. 10) with minimal changes to the speciation⁷⁹ (Fig. 11) or electrochemical characteristics.³² However, this adds an additional component to the DES system and, at sufficiently high-water contents, the properties of the DES are lost and it resembles an aqueous system.²¹ However, there are examples of the deposition of Cu,³³ Ni³² and Cr³⁴ where the water content is of the order of 5–15 wt% and it has been demonstrated in electroplating trials³⁷ that water contents as high as 5 wt% do not significantly impact the process. Obviously, the deposition of reactive metals (e.g. Al and Mg) would require a negligible water content and must be performed in a glovebox.

Despite the relative insensitivity of DES-based metal finishing processes to water, it is clear that it would have to be monitored and controlled in an industrial setting. Processes would have to be performed in open tanks where water absorption would be inevitable and the extent of water incorporation would vary with temperature, surface area and humidity.^{32,78} Water content in the DES can be conveniently measured by a variety of methods such as K-F titration^{32,34,78} and NIR spectroscopy,⁷⁷ but controlling it would be complex.

Anode reactions.—While most studies have concentrated on cathodic processes associated with metal deposition, the characteristics of the anode reaction should not be ignored.^{8,9,12,17} The use of

a soluble anode is preferred as it assists in maintaining a constant metal ion concentration and avoids the anodic breakdown of the DES. The DES material does provide some advantages in that it tends to prevent passivation of the anode.^{9,17} However, one problem is that in some systems (e.g. containing Fe³⁺, Cu²⁺ and Cr³⁺) the anode can be corroded by a comproportionation reaction.^{34,80} This increases the current efficiency of the anode reaction, introduces species into the plating solution in lower oxidation states (e.g. Fe²⁺, Cu⁺ or Cr²⁺) and depletes the solution of higher-valency species that normally deposit. These effects can cause serious issues with process control. Even in systems where anode corrosion is not possible it is still necessary to ensure that its anodic current efficiency is close to 100% and there are no side reactions.

The use of insoluble anodes (e.g. DSA, Pt or C) is even more problematic as they will typically involve the breakdown of the DES components.^{8,17,21,81,82} Potentially some of these anode products could be toxic and, even if they are benign, their gradual accumulation may have a significant influence on the deposition process and the DES may need to be periodically regenerated.^{20,21} In one study of zinc deposition from ethaline, the formation of various chlorinated organic compounds (but not Cl₂) was observed at the anode, compromising the “greenness” of the process.²¹ The addition of water prevented the formation of chlorinated products but other complex organic compounds were produced in their place. Notably if the cathodic and anodic reactions involve processes other than metal deposition and dissolution, the breakdown of the DESs into complex and possibly toxic products is inevitable.

An instructive example related to anode selection was the development of a pilot scale process to deposit hard chromium on to steel substrates from a type I DES.³⁴ Initially an insoluble DSA type anode was employed and the main reaction occurring was the evolution of Cl₂. This required local exhaust to dissipate, and was obviously in conflict with the process being “green.” When soluble anodes were substituted, Cl₂ was not evolved but it was found that the anode was corroding (by comproportionation) while being anodically dissolved. Therefore, Cr was being generated at the anode more quickly than it was consumed at cathode and the overall rise in the Cr concentration significantly increased the viscosity and conductivity. The use of soluble anodes therefore complicated the control of the plating bath chemistry.

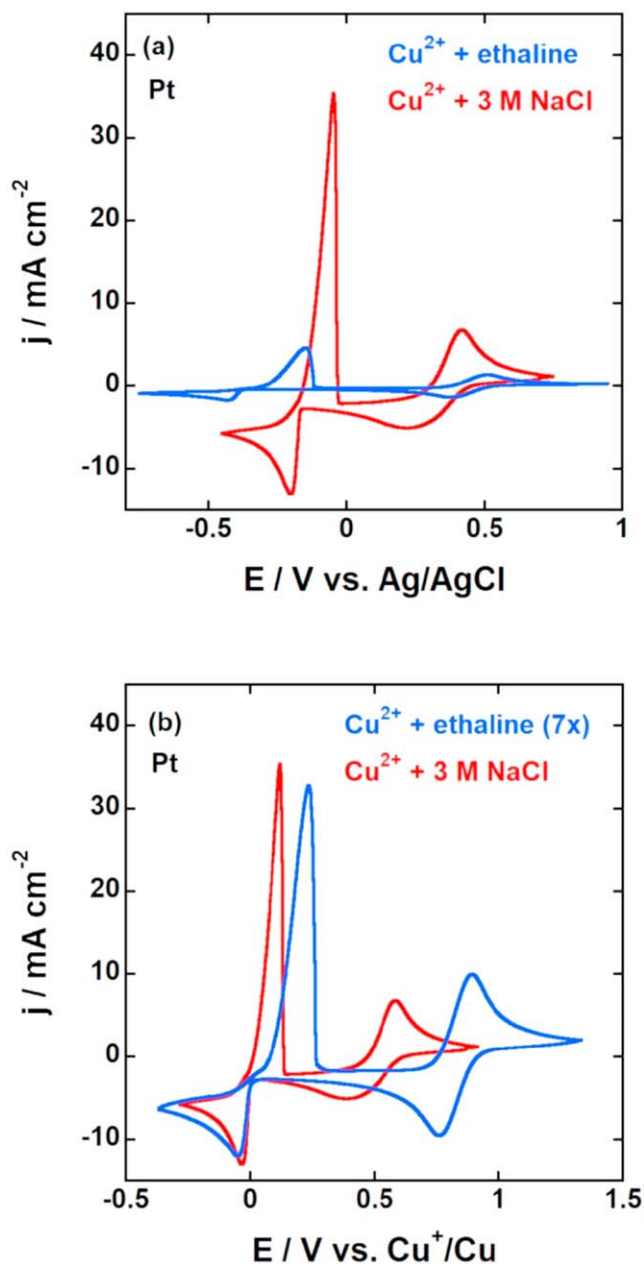


Figure 8. Cyclic voltammograms of 0.1 M CuCl_2 in ethaline (4.3 M Cl^-) and 3 M NaCl at a Pt electrode at a scan rate of 20 mV s^{-1} indicating similar speciation and electrochemical behaviour. (a) CVs plotted against Ag/AgCl reference electrode (b) CVs plotted against the onset potential for Cu^+/Cu reaction where the ethaline data has been rescaled by a factor of seven. Reprinted with permission from Ref. 66. Copyright 2020 American Chemical Society.

Main Barriers to Adoption—Process Scale up

In this final section, barriers related to the scale-up of DES surface finishing process are discussed. These are issues that do not manifest themselves at the laboratory scale, but become more important as the technology readiness level (TRL) increases.

Limited demonstrations at pilot scale.—One issue preventing the adoption of DES-based metal finishing processes is that most processes have been demonstrated at a relatively low TRL. These typically correspond to “experimental proof of concept” (TRL 3) or “technology validated in lab” (TRL 4). These studies do not provide sufficient evidence that technologies will work at scale in an

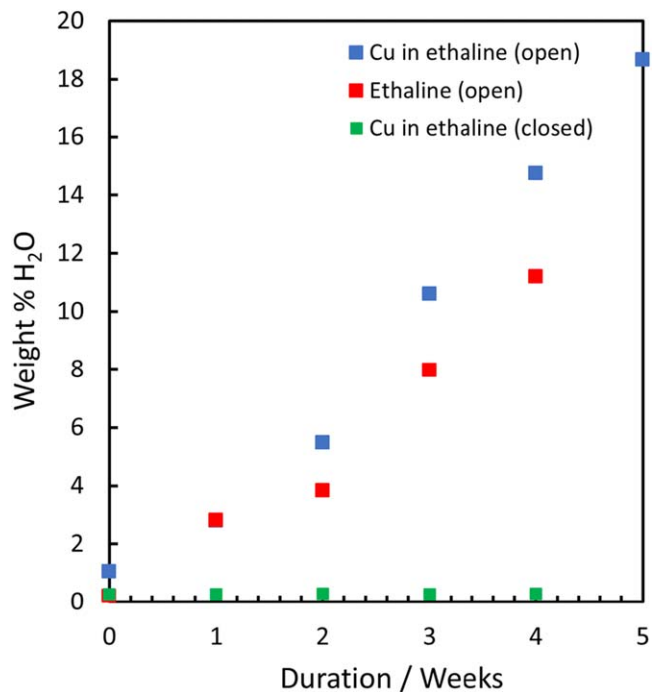


Figure 9. Water uptake from ethaline containing solutions exposed to air (open) or covered (closed). Saturation occurs after 8 weeks. Data taken from Ref. 77.

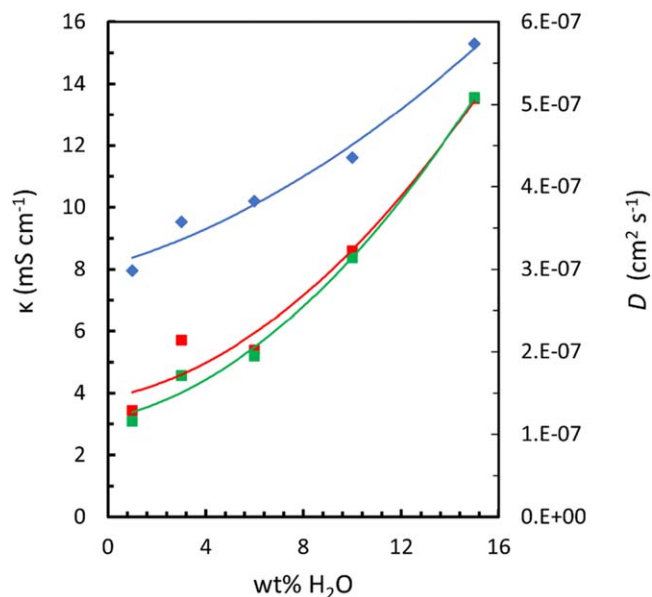


Figure 10. Specific conductivity, κ , (◆) as a function of water content (wt %) in ethaline containing 0.20 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 25. Also shown are the diffusivity, D , of $[\text{CuCl}_4]^{2-}$ (■) and $[\text{CuCl}_2]^-$ (●) species as a function of water content. Data taken from Ref. 33.

industrial setting. This issue has been raised by Binnemans in relation to ionometallurgy processes using DESs, with most process demonstrations corresponding to TRL 2 – 3 and only one relevant example at TRL 6.²⁰

Table IV summarises the pilot scale metal finishing process that have been undertaken using DESs and includes examples of the electrodeposition of metals and alloys, electroless processes and electropolishing. The majority of the studies were funded under an EU program (IONMET) or Innovate UK grant and generally correspond to TRL 6 (“technology demonstrated in relevant environment”)

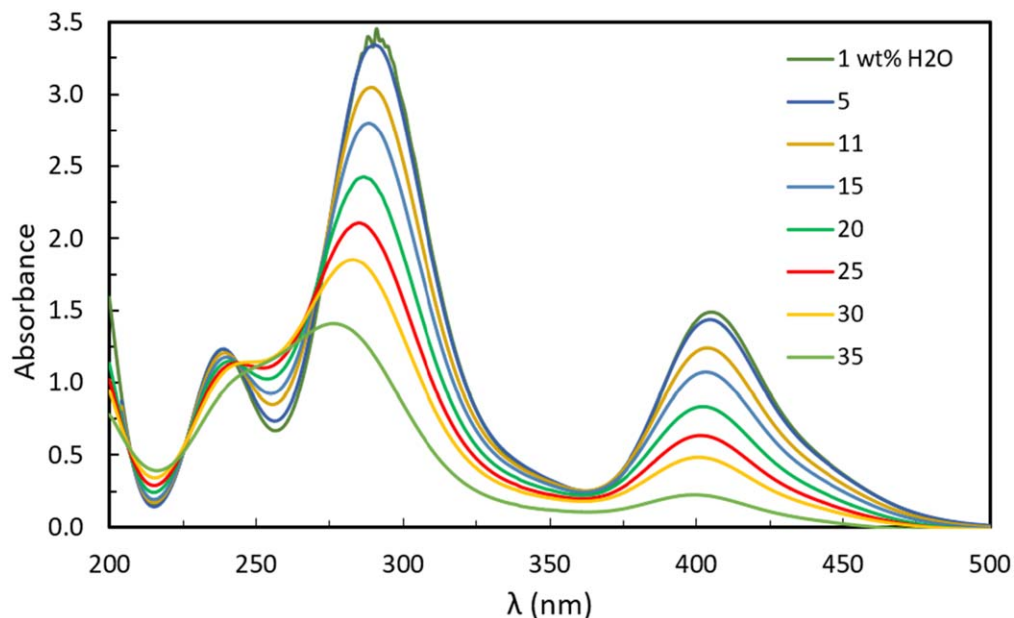


Figure 11. UV-vis spectra of 0.05 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in ethaline system at 1–35 wt% H_2O . Up to a water content of 5%–10% there are very minimal changes in copper speciation. Adapted from Ref. 77.

Table IV. Summary of main characteristics of scaled-up metal finishing processes employing DES and ILs. Capacity reflects total volume of all tanks involved in the process and gives an indication of overall scale. TRL is an estimate of the technology readiness level.

Process	Metal / Alloy	DES / IL Electrolyte	Process	Capacity (liters)	TRL	References
ED	Al	[EMIm]Cl- AlCl_3	Plating module only	100	4	12,17
ED	Cr	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in ChCl	Rack plating, pre and post treatment	1300	7	34
ED	Zn/Sn	ZnCl_2 and SnCl_2 in ChCl:EG (1:2)	Barrel plating, pre and post treatment	400	6	12,17
ED	Zn/Ni	ZnCl_2 and SnCl_2 in ChCl:EG (1:4)	Barrel plating only	150	5	54
EL	Ag	AgCl in ChCl:EG (1:2)	Electroless, pre and post treatment	750	6	83
EP	SS	ChCl:EG (1:2)	Electropolish, pre and post treatment & recycle	1300	6	12,17

with one industry-based project related to hard chromium plating at TRL 7 (“system prototype demonstration”). Details of these pilot-plant studies and some preliminary results are discussed in various research publications^{34,54,83} and review articles.^{3,9–13,17} Notably, some of these comprised complete plating lines which fully integrated cleaning, pre-treatment, plating rinsing and drying steps, while others addressed only the deposition or polishing steps. Figure 12 illustrates some examples of these various pilot scale trials.

It has been suggested^{11,12} that DES based processes can be considered “drop-in replacements” for some existing aqueous-based processes. While this might be the case for some of the simpler finishing processes (e.g. electroless deposition or electropolishing) it is more likely that significant modifications would be needed to accommodate the unusual properties (e.g. high viscosity, low conductivity, differing materials compatibility) of the DES. For example, pumps and pipework would have to be modified or upgraded, along with agitation systems to accommodate the high viscosity electrolyte. Other process steps involving pre-treatment, rinsing, drying, and recycling or disposal of DESs would also require substantial changes. A 2019 study on pilot-scale chromium plating from a DES, gives a clear idea of the modifications needed to adapt an aqueous plating line to a DES-based process.³⁴

These studies are useful as they indicate the requirements for process scale up and some of the issues faced, but lack the critical information needed to take the process to a higher TRL. This would include, for example, a detailed analysis of material and energy balances, CAPEX and OPEX calculations, a life-cycle analysis and

information on DES recycling.²⁰ Broadly speaking, the metal finishing community does not seem to be convinced by these initial pilot scale trials and there is a perception that the disadvantages outweigh any advantages. Currently there do not appear to be any examples of large-scale processes that have been implemented and are commercially viable, although it is still possible that these will eventually emerge.

Material costs and supply.—A significant impediment to the adoption of DES or IL-based processes in metal finishing relates to their high costs. In particular, the use of ionic liquids can be largely discounted on the grounds of their prohibitively high costs (>US \$200 per kg). In contrast, DESs are much less expensive and prices for quantities of 50–1000 kg from a commercial supplier (Scionix Ltd) in 2019 were £30 (US\$40) per kg, although this is still expensive compared to various acids and salts used to formulate electrolytes for aqueous processes. For example, concentrated phosphoric or sulfuric acid used in electropolishing process has a cost (\$2,000 - \$4,000 per ton) compared to an estimated \$40,000 per ton for a DES. Similarly, in a pilot scale study of Zn-Ni plating, the high cost of the DES was given as a reason not to develop the process further.⁵⁴ The cost is less important if the DES can be recycled but, as they are mixtures and have a high viscosity and low vapour pressure, this is challenging.²⁰ There have been some limited trials of DES recycling, but rarely at the pilot-plant scale.¹⁷ Another concern is that there appears to be no current supplier of DES materials at the kg or ton scale, although these exist for ILs.



Figure 12. Examples of scaled-up DES processes reported in the literature. (a) Cr plating (b) Zn-Sn plating; (c) Zn electrowinning (d) Al plating (e) Ag immersion plating (f) stainless steel electropolishing. See Table IV and the main text for additional process details. Reprinted from Ref. 5, Copyright (2022) with permission from Elsevier.

Energy requirements.—There has been no direct analysis of the energy requirements of DES-based processes versus aqueous ones, but it is possible to make some generalisations related to this issue. In terms of electrical power consumption, this would depend on the anode and cathode reaction characteristics (e.g. equilibrium potentials and overpotential, current efficiency) but would likely be dominated by ohmic losses in the electrolyte. As DES materials have a conductivity at least ten times lower than for aqueous electrolytes, this would drastically increase the power consumption at the same applied current density. It might be argued that if the process needs to operate at elevated temperatures, this resistive heating is not really wasted, and reduces the duty of immersion heaters. However, in some situations excessive heat dissipation by Ohmic effects may require additional cooling,⁸ and such issues have been reported for Cr plating from a low conductivity DES.³⁴

Some additional energy savings might be possible as the negligible vapour pressure of DESs may make an exhaust system redundant, but this would require that toxic products are not generated at the anode or cathode.²⁵ On the other hand, if the process has to be run at elevated temperatures to maintain a conductivity and fluidity comparable to aqueous systems, this will also increase energy use. Additional complexities in comparing energy consumption arise as DES and aqueous systems have different heat capacities, thermal conductivities and rates of evaporative losses. In the absence of any comparisons, it is difficult to say what the energy requirements for a DES process would be higher or lower, and this uncertainty represents an additional barrier to adoption.

Materials compatibility and corrosion.—It is generally assumed that most commonly used DESs are non-corrosive to most metallic materials that might be encountered in metal finishing operations. In support of this, some limited corrosion testing has been performed on iron, nickel, aluminium, stainless steel and aluminium alloys.^{84,85} This testing generally shows that the corrosion rate is very low (10^{-3} to 0.1 mmpy) which likely reflects that DESs typically have a neutral or slightly acidic pH (Table II) and the low concentrations and diffusivities of oxidising species such as O_2 and H^+ .^{84,85} Only acidic DESs such as maline and oxaline have appreciable corrosion rates. Note that this is an assessment of general (uniform) corrosion

and susceptibility to localised corrosion (pitting and SCC) has never been examined.

However, the corrosivity of DESs containing certain metals salts (e.g. $CrCl_3$, $CuCl_2$, $FeCl_3$) is much higher and we have observed that these can attack many metals and alloys including stainless steels. These salts are strong oxidants, and in aqueous solutions and are used to etch metals at high rates.⁴⁹ In a previous study we have shown that corrosion rates in aqueous and DES media due to these oxidants is typically 10–100 times higher than for O_2 induced corrosion.^{80,86} It has been reported that DESs formulated for $CrCl_3$ and choline chloride for hard chromium plating was highly corrosive to many metals and alloys (including stainless steel) and only pure titanium showed sufficient resistance to be used.³⁴ The high corrosivity of these DES electrolytes should be kept in mind when designing plating installations.

The chemical compatibility of DESs with polymeric materials used to fabricate tanks and pipework has been tested in some pilot studies.^{12,17,34,82} It appears that most common plastics (PE, PP and PVC) have good compatibility in most DESs, but in one study³⁴ more costly fluorinated polymers (PTFE and PVDF) were preferred. For elastomers, some compatibility issues have been reported in strongly oxidising solutions and fluorinated materials are recommended.^{12,82} Again, the data on corrosion and materials compatibility for DES material is incomplete and largely unexamined. This is in contrast to conventional salts, solutions and solvents where such data is readily available.

DES processes often have viable alternative.—Some scaled-up DES processes have been developed to address an existing problem in the metal finishing industries, even when there appear to be viable aqueous alternatives. A good example is the proposed electrodeposition of chromium from DESs using a Cr(III) process. The justification for this is the toxicity of Cr(VI) processes and looming REACH restrictions,⁸⁷ but aqueous-based trivalent chromium processes for hard chrome have been commercially available since 2017 and even longer for decorative chrome. The development of aqueous Cr(III) processes was difficult and prolonged, but was achieved by reformulating the electrolytes⁸⁸ and in some cases by using pulse plating.⁸⁹ Similarly, the motivation for another DES project⁵⁴ was to deposit Zn-Ni alloys from a DES as a replacement for toxic

cadmium plating, but once again there are commercially available aqueous processes to perform Zn-Ni plating.

Conclusions


In this article we have summarised the main barriers to the adoption of DESs in the surface finishing industries and discussed each of them at length. Additionally, we have identified some key limitations of DES materials that are not commonly discussed in the literature, and have also drawn from the experiences in related fields (ionometallurgy) where similar issues have presented themselves. The severity of these barriers varies, but in some cases (e.g. low deposition rate, poor throwing power, cost and sustainability concerns) are particularly critical and act as strong disincentives to adopting DES processes. In other cases, the barrier can be mitigated or overcome, but may introduce additional issues or complexities. To some degree these barriers also depend on the type of finishing process and choice of DES, but there appears to be no combination of these which resolves all the issues.

Importantly, attempting to replace existing aqueous metal finishing processes with DES-based ones would appear to be a difficult task, even if comparable or superior performance and characteristics could be demonstrated. This alone is not likely to lead to its adoption in industry, especially if the process is likely to be more complex and expensive than aqueous ones. It would be more prudent to concentrate on metal finishing processes which cannot be achieved using aqueous systems, and where approaches based on ionic liquids might be too expensive. This immediately brings to mind reactive and refractory metals such as Al, Mg, W, Ta and Ti as suitable candidates.

What of the future? It is our belief that, unless these barriers can be overcome, DESs will never be seriously considered for adoption in the metal finishing industries. However, it seems likely that academic studies of electrodeposition and electropolishing from DESs will continue unabated. There are a large number of possible DES systems, and an even larger number of metals and alloys that can be deposited or polished, so that the topic is practically inexhaustible. While this may lead to useful data on these electrochemical systems, these activities are unlikely to enable any practical metal finishing applications. It may be that DESs with improved properties will be eventually developed, but it will be challenging to achieve the low fluidity required to ensure high deposition rates and throwing power, and meet other constraints related to greenness, sustainability and cost. However, the possibility remains that some niche surface finishing application will eventually be identified that DESs can fulfil, and similarly, we do not rule out that DESs will have significant uses in other applications areas, where many of these constraints have less relevance.

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