



## The use of ionic liquids based on choline chloride for metal deposition: A green alternative?

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### ABSTRACT

Ionic liquids are studied intensively for different applications. They tend to be denoted as “green solvents”, largely because of their low vapour pressure. In recent years toxicity and biotoxicity of ionic liquids have also been investigated, which proved that not all of these are “green”. In this paper the use of ionic liquids based on choline chloride and ethylene glycol in electrochemistry is discussed in the context of their use as green solvents. Due to their low toxicity and ready biodegradability, these deep eutectic solvents are promising for the electrodeposition of metals. The influence of the use of these liquids as metal deposition baths on the waste water is investigated. Drag-out was found to be the most influencing parameter on the environmental impact of the process, as it is three times higher compared to classical solutions due to the higher viscosity of the ionic liquid. There are no major changes needed in the rinsing configuration of classic electroplating plants, and ion exchange to remove the metal out of the waste water was not hindered by the presence of the ionic liquid. The formation of by-products during the deposition of metals has to be further investigated and evaluated in consideration of the environmental impact.

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### 1. Introduction

The interest in ionic liquids and especially in room temperature ionic liquids has increased enormously in the last decades. They are studied in a broad range of different applications, from their use as solvent for organic synthesis and biological reactions due to their low volatility (Seddon and Holbrey, 1999; Dupont et al., 2000; Trissa et al., 2005; Forbes et al., 2006) over material separation processes to electrochemistry (Buzzeo et al., 2004; Endres, 2004; Fernicola et al., 2006; Galinski et al., 2006).

One of the applications of electrochemistry is electrodeposition of metals or electroplating (Endres, 2002). The electroplating industry traditionally uses aqueous solutions, because of the high solubility of electrolytes and metal salts, resulting in highly conducting solutions. However, water has a relatively narrow potential window, and hence the deposition of some metals is hindered by poor current efficiencies and/or hydrogen embrittlement of the

substrate. The main driving force for non-aqueous electrolytes has been the desire to deposit refractory metals such as Ti, W and Al (Abbott and McKenzie, 2006). The key advantages of ionic liquids in this area are their wide potential electrochemical window, the high solubility of metal salts, the absence of water and metal/water chemistry and the high conductivity compared to non-aqueous solvents (Endres & Zein El Abedin, 2003; Endres, 2004; Endres et al., 2006; Steward et al., 2004; Abbott and McKenzie, 2006; Galinski et al., 2006).

Although it may be difficult to compete with existing plating systems for common applications in terms of economy, ionic liquids can provide an alternative for metals that are difficult to plate. In addition, ionic liquids are also a viable alternative to environmentally hazardous processes such as the use of chromic acid for the electrodeposition of chromium, the use of cyanides in silver plating, or the replacement of Cd-coatings ([www.scionix.co.uk](http://www.scionix.co.uk), 2007).

Although ionic liquids reduce the gaseous emissions compared to VOCs, some aspects should be taken into consideration before they can be called “green solvents”. Only few studies about the environmental impact of ionic liquids have been published and only few toxicological and/or ecotoxicological data are available.

Magginn et al. (2006) present toxicity experiments indicating that ionic liquids (pyridinium and imidazolium based) are more

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### Nomenclature

$z_n$	concentration in the tank, after the $n$ th rinse (g/L)
$c_n$	concentration on the work after the $n$ th rinse (g/L)
$c_0$	concentration in the initial bath (g/L)
$k$	$D/V$ (1/s)
$t$	time (s)
$D$	drag-out (L/s)
$V$	rinse volume (L)
$Q_r$	flow rate in the rinse tank (L/u)
$Q_c$	flow rate in the cascade rinse (L/h)
$V_d$	volume of drag-out (ml)
$C_r$	concentration in the rinsing solution (mg/L)
$V_r$	volume of the rinsing solution (L)
BV	bedvolume
E	Evaporation (L/h)

toxic than common organic solvents. They found also a distinct effect of the chain length of the alkyl residues of imidazolium based ionic liquids on toxicity as did others before (Jastorff et al., 2003; Rogers et al., 2003; Pernak et al., 2004; Ranke et al., 2004).

In this paper the environmental impact of a choline chloride based ionic liquid, Ethaline200, in electroplating applications will be studied. Ethaline200 consists of ethylene glycol as hydrogen donor and choline chloride. As both components of Ethaline200 are not harmful for the environment (Staples et al., 2001; Switzenbaum et al., 2001; UNEP, 2004) and readily biodegradable, no adverse effects of Ethaline200 are to be expected.

As Ethaline200 is readily biodegradable, the main environmental impact is related to the presence of heavy metals in the rinsing solutions and to products formed during electrolysis due to incomplete current efficiency at the cathode and anode reactions.

Ionic liquids based on choline chloride have the additional advantage to be easy to prepare, to be water and air stable and to be cheap, which enables their use in large scale applications (Abbott et al., 2001). Abbott et al. have described different types of ionic liquids based on choline chloride and their applications (Abbott et al., 2001, 2005, 2006, 2007).

During surface treatment with process solutions, a film of the bath solution remains on the parts and on the rack or barrel. The bath solution also remains in cavities and gaps, and is transferred into the following baths. Due to this transfer, the chemicals of the process are lost and should be replenished. All process solution lost in this way is defined as drag-out (Jansen and Volk, 2002).

Not only does the drag-out lead to consumption of electroplating solution, in the surface finishing processes drag-out is also the source of pollutants in the rinsing water. The mass of pollutants in drag-out is equal to the mass of pollutants in the rinse discharge (Robinson et al., 1999). The arrangement of the rinse tanks and the rinse flow does not change the total mass of contaminants released but only the concentration and volume of the waste. The drag-out rate is one of the factors influencing the optimal rinse configurations. Other factors include the evaporation in the plating tank, the required quality of the final rinse water, and cost for water and waste water treatment or disposal (Cushnie, 1994).

Drag-out reduction techniques provide two primary benefits: they reduce process chemistry loss and take full advantage of the rinse water reduction opportunities. Drag-out also depends on solution properties like density, viscosity and surface tension. As bath chemistry and temperature can change viscosity, these parameters influence the volume of drag-out as well.

Some drag-out predictions can be found which include some of the drag-out influencing parameters described above. However,

most perform poorly in predicting drag-out for a variety of electrolytes. In spite of numerous attempts, an accurate model could not be found (Robinson et al., 1999).

## 2. Methods and materials

### 2.1. Reagents and solutions

ZnCl<sub>2</sub> (Acros, >98%), NH<sub>4</sub>Cl (VWR, >99%) and ZnSO<sub>4</sub> · 7H<sub>2</sub>O (Acros, >99.5%) were used as received. Choline chloride solution 78% (Taminco) was dried for 1 week in an oven at 70 °C and subsequently placed in a desiccator to allow cooling down and crystallising and to avoid water uptake by hygroscopic properties of the choline chloride salt. Ethylene glycol (Chemlab, >99%) was used as received.

The eutectic mixture Ethaline200 was prepared by stirring the two components choline chloride and ethylene glycol in a 1:2 molar ratio at 70 °C until a homogeneous colourless liquid was formed. The liquid was allowed to cool down and transferred to a dark coloured flask for storage.

Five standard solutions were used in the experiments. These are:

- “Solution 1” refers to a 500 ml aqueous acid zinc bath made up by adding 75 g NH<sub>4</sub>Cl and 50 g ZnCl<sub>2</sub> to 500 ml of water in a beaker;
- “Solution 2” refers to a 500 ml Ethaline200 bath containing 1 M Zn<sup>2+</sup> prepared by dissolving 143.75 g ZnSO<sub>4</sub> · 7H<sub>2</sub>O in a beaker with 500 ml Ethaline200;
- “Solution 3” refers to a 2.5 L aqueous solution containing 200 mg/L Zn, prepared by dissolving 2.20 g ZnSO<sub>4</sub> · 7H<sub>2</sub>O in 2.5 L deionised water;
- “Solution 4” refers to a 2.5 L aqueous solution containing 200 mg/l Zn, prepared by diluting 7.7 ml of the 1 M ZnSO<sub>4</sub> · 7H<sub>2</sub>O solution in Ethaline200, from the drag-out experiment described under point 7, to 2.5 L using deionised water;
- “Solution 5” refers to a 1.5 L Ethaline200 solution containing 200 mg/L, prepared by dissolving 2.637 g ZnSO<sub>4</sub> · 7H<sub>2</sub>O in 1.5 L Ethaline200.

### 2.2. Determination of zinc in solution

The concentration of zinc in solution was determined using a flame atomic absorption spectrometer (AAS) (SOLAAR, UNICAM 989) with a detection limit of 0.008 mg/L and deuterium background compensation. The standard solutions were made by dilution of a 1000 mg/L zinc standard solution (Merck Titrisol Zinc Standard).

### 2.3. Experimental determination of drag-out

For the drag-out test, a brass plate with a surface of 1 dm<sup>2</sup> and 0.3 mm thick was thoroughly cleaned, etched in 1 M H<sub>2</sub>SO<sub>4</sub> and rinsed with deionised water and acetone, and dried for 5 min in an oven at 70 °C. The brass plate was then immersed in the solution (either solution 1 or 2) for 60 s. The plate was slowly removed vertically out of the bath and was held for 10 s above the plating bath. Then the plate was immersed in a beaker containing 400 ml deionised water. The water was agitated by using a rod and the plate was agitated manually for 60 s. The plate was then withdrawn from the beaker and held above the surface and rinsed with 10 ml of deionised water and given 10 s to drain. The deionised water was transferred analytically to a 500 ml volumetric flask and the flask

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