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Effect of excess hydrogen bond donors on the electrode-electrolyte interface between choline chloride-ethylene glycol based solvents and copper.

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Abstract

The fine tuning of deep eutectic solvents (DES) via the addition of co-solvents such as water or excess ethylene glycol, to improve the electrodeposition of metals is becoming increasingly common. However, as these changes become commonplace, our understanding of their effect must deepen as well. In this work, we look into how water, a secondary hydrogen bond donor (HBD), added to choline chloride:ethylene glycol (1:2 ChCl:EG) DES changes the electrochemical behaviour of the solution. We use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to identify and map the organic molecules that have interacted with the surface. A copper surface was used as an electrochemically active substrate. The molecular maps provide insights into how solvent composition changes electrolyte reactivity, as well as showing the main driver behind the entrapment of organic compounds in metal deposits from DES. This behaviour was studied at different potentials based on the information provided by linear sweep voltammetry data of the copper in the solution. These results are then contrasted against a 1:4 ChCl:EG
solution, where the excess ethylene glycol acts as secondary HBD, in order to determine the individual contributions of the co-solvents and how they affect the electrochemistry of the media and their reactions with the copper electrode. This information can be used as a set of guidelines for the tuning and optimisation of ethylene glycol based DES for metal deposition.

Keywords: Time-of-flight secondary ion mass spectrometry, Non-aqueous solvents, Copper

1. Introduction

Deep eutectic solvents (DES) are a tunable and sustainable low-cost alternative to ionic liquids [1, 2, 3] with a variety of applications in electrochemistry such as the electrodeposition of metallic nanoparticles and coatings [4, 5]. The existence of DES relies on strong interactions between their components to lower the melting point and form a stable liquid phase. Typically, a quaternary ammonia salt such as choline chloride acts as a hydrogen bond acceptor (HBA), and an organic molecule like ethylene glycol (EG) as a hydrogen bond donor (HBD). DES are water stable and hydrophilic [6], which makes their transition into industrial scale applications much smoother than ionic liquids based technologies. Water, among others, acting as a secondary HBD or co-solvent can be used to improve and fine tune the desirable properties of the DES [7, 8]. Every change in the composition of the DES increases the complexity of the behaviour of these mixtures. Thus, a fundamental understanding of the interactions involved between the tuned DES and metals is of great importance. In this work, we focus on how these added HBDs can affect the species that are formed and how they bind with the electrode
Conductivity, viscosity and electrochemical window are the most commonly tuned properties in DES for electrodeposition [5, 9, 10, 11]. In order to reduce the viscosity and increase the conductivity co-solvents like water and ethylene glycol are added to the DES. The addition of 1 mol eq (6.5%w) of water reduced the viscosity by 30% and increased the conductivity by 40% [12] through the disruption of the hydrogen bonds between the components. On the other hand, water can limit the electrochemical performance of the electrolyte, as hydrolysis and water-choline reactions take place on the electrified interface [13, 14, 15]. An alternative to water is the use of ethylene glycol. Miller et al. [11] improved the electrodeposition yield of iron by increasing the ratio of ethylene glycol to choline from 1:2 to 1:4. Although the conductivity of the 1:2 and 1:4 solutions did not increase, it is still unknown if any parallels can be made between the addition of water and ethylene glycol as co-solvents and what are their individual contributions to the properties of the solvent.

The changes in the electrolyte when water is added to DES have been approached in a multitude of ways, such as: Brillouin spectroscopy [16], Pulse-field gradient nuclear magnetic resonance (PFG-NMR) [6, 17]. Neutron diffraction [18] and contact mode atomic force microscopy [19] have been used to focus on the electrode-electrolyte interface of non electrochemically active surfaces e.g graphite, platinum. Some studies on the effect of the addition of water report the occurrence of microscopic phase segregation between aqueous and DES phases [14, 16, 19, 20]. This could mean that there is more than one electrode-electrolyte interface, leading to different reactions with
the electrode surface.
On the other hand, the interactions between metal surfaces and DES, have been probed by inductively coupled plasma optical emission spectrometry (ICP-OES) and total organic carbon (TOC) for the electrolyte. The electrodes were studied using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)[21]. In this work, copper was chosen as model electrochemically active surface and its reactions with the segregated aqueous and DES phases can be studied through the use of time-of-flight secondary ion mass spectrometry (ToF-SIMS). The effects of DES on the morphology and the different reactivities of copper have been shown by Gosh et al and Gu et al.[22, 23]. In those works, the effect of solvent decomposition and the role of additives such as ethylene diamine (EDA) on the deposition of copper, were studied, but the question of the mechanism by which EDA, affect the deposition, and the effect of the electrolyte decomposition on the deposits remain open. In a previous study[24], we have shown the advantages that ToF-SIMS offers to the study of the interface in DES between adsorbed species and an electrochemically inactive electrode (glassy carbon). Tof-SIMS provides detailed mass spectra of µm areas of the top 5 nm of the surface which allows us to distinguish between multiple interfaces and any separate reactions on that happen with copper.

Our work on glassy carbon showed how the presence of excess ethylene glycol changed the decomposition route and by-product accumulation of DES on an electrochemically inactive surface. In some cases, DES without excess HBD, accumulated on the surface in response to potential, inhibiting the deposition of metal and inducing corrosion on the deposit. On the other hand,
this adsorption of organics could be avoided by using larger amounts of EG. In this system, the choline is less likely to accumulate but the decomposition route changes preferring an electrochemical decomposition over a Hoffman elimination. In this work, we focus on how choline and its decomposition products interact with a copper substrate and the role of increasing amounts of water on the reactivity. In order to distinguish the contributions of water, we compare the performance of the DES to a similar mixture (1:4 ChCl:EG) where excess amounts of ethylene glycol acts as secondary HBD.

2. Materials and Methods

Choline chloride (Sigma-Aldrich, >98%) was mixed with ethylene glycol (Merck, 99.5%) in molar ratios 1:2 and 1:4. The mixtures were stirred and kept at 80°C for 6 hours and nitrogen gas was bubbled through the solution before the experiments. A Karl Fischer coulometer was used to control the water quantity before each experiment and an average value of (1.0 ± 0.1) weight % of water was obtained. Deionised water was added afterwards and stirred until thoroughly mixed. The solutions are refered to as: (1:2LW) for the 1:2 ChCl:EG solution with 1% water; (1:2HW) for 1:2 ChCl:EG solution with 10% water and finally 1:4 for the 1:4 ChCl:EG solution. Copper (>99%) was used as the electrode material. The electrochemical experiments were done on a 3mm diameter disc mounted in resin for the linear sweep voltammetry and 10x35 mm plates were used for the ToF-SiMS analysis. All samples were polished with 0.05 μm alumina, dipped in pickling solution (10%HNO₃, 1% HCl) for 1 minute before deposition, and then rinsed with methanol. Linear sweep voltammetry (LSV) and chonoamperometry (CA) measurements
were performed in an electrochemical cell with a three-electrode configuration, consisting of a silver wire quasi reference electrode (Ag/AgCl QRE), a dimensionally stable counter electrode, made of titanium oxide covered with ruthenium indium titanium oxides, and a copper working electrode. All the potentials mentioned throughout the manuscript refer to Ag/AgCl QRE constructed by inserting a chloridised silver wire into a fritted glass capillary filled with 1:2 molar ratio choline chloride to ethylene glycol. LSV was done between OCP and -1.15 V vs Ag/AgCl QRE at 1 mV/s for all solutions. CA measurements were done at selected potentials for 600s, in order to ensure steady state conditions. The samples were then rinsed repeatedly with water and methanol and air dried.

ToF-SIMS measurements were performed with a TOF.SIMS 5 instrument from ION-TOF GmbH (Münster, Germany). Positive ion mass spectra were acquired using a 30 keV Bi\(^{3+}\) primary ion beam operated in the high current bunched mode for high mass resolution (approximately 8000 at 29 µm (\(^{28}\)Si\(^{+}\))). In this mode, a lateral resolution of 3 µm is achieved, with a surface sensitivity of 1-5nm. The pulsed ion beam target current was approximately 0.60 pA. Large area images were acquired following the protocol described in Gamarra et. al. [24]. Deviations (either negative or positive) with an absolute value below 50 ppm are indicative of good assignments. In each spectrum or image, intensities are normalised to the total ion intensity, to reduce topographic and matrix effects. This allows for a relative quantification between samples with similar chemistries [25, 26].
3. Results

3.1. Linear Sweep voltammetry on copper electrodes in the ChCl:EG based electrolytes

The electrodes were polarised from their open circuit potential (E\(_{OC}\)) to -1.2V (vsAg/AgClQRE), when the reduction of hydroxyl groups becomes the dominant reaction\[27\], via linear sweep voltammetry. The current density measured on the Cu surface approaches -1.0x10\(^{-3}\)A/cm\(^2\) (figure 1), which fits one of the definitions used for electrolyte decomposition \[28\].

Based on the voltammograms presented in figure 1, different polarisation potentials were chosen to study the interactions between electrolyte and electrode surface. First, at the open circuit potential (E\(_{OC}\)), any electrode-electrolyte interaction will come only from the affinity between solvent and electrode. As the potential becomes more negative, -0.60V was chosen as there is a reduction process on copper for the 1:4, that is absent in 1:2 regardless of the water content. After this, a third potential was chosen at -0.95V because at this point, the 1:2HW shows the onset of a reduction reaction. This is in accordance with the literature reports of a reduced electrochemical window in the presence of water, due to hydrolysis \[27, 29\]. Finally, at -1.15 V vs QRE, all the available OH- groups from water and the electrolyte are being electrochemically reduced. These electrochemical profiles provide the framework for the ToF-SIMS analysis.
3.2. Study of the potential dependent interactions between Copper electrodes and ChCl:EG Solutions

Copper electrodes were immersed in ChCl:EG mixtures for 600s under varying polarisation potentials i.e., open circuit potential ($E_{(OC)}$), -0.60V, -0.95V and -1.15V. The choice of fragments and common contaminants on ToF-SIMS spectra are treated the same way as in previous work [24]. Figure 2 shows an overlay of ToF-SIMS mass spectra acquired from large area (1 mm x 2.5 mm) imaging on an exposed copper substrate at ($E_{(OC)}$). Sodium and ($SiC_3H_5^+$) polydimethylsiloxane are common contaminants, but do not overlap with any fragment of interest, and therefore are of no concern.
This analysis is divided in 2 sections. The first section focuses on the copper containing compounds found on the surface. These will be used to determine how an electrochemically active surface interacts with the different electrolytes. The second section focuses on the changes in the molecular fingerprint of the electrolyte, which covers choline and ethylene glycol derivatives, to provide information on possible interactions not involving ionic interactions with the surface.
3.2.1. Effect of the electrolyte on the electrode surface

ToF-SIMS data analysis focused on copper containing compounds was performed, in order to evaluate the effect of the DES on the working electrode surface. Table 1 shows the most relevant fragments for this analysis. First, the presence of copper molecules proves that the surface of the electrode is being probed. Cu\(^+\), with a nominal mass of 62 m/z, is shown as a reference. Next, \(CuC_2H_4O_2^+\), with a nominal mass of 122 m/z, is representative for ethylene glycol-copper complexes formed during the corrosion of copper by ethylene glycol in the presence of chlorides [30]. Additionally, the common corrosion product \(Cu_2OH^+\), with a nominal mass of 142 m/z was also recorded. Finally, copper bonded to choline and its byproducts was found in the form of \(C_5H_{13}NOCu^+\) and \(C_5H_{11}NCu^+\), with nominal masses of 166 and 148 m/z respectively. The proposed structures for these fragments are presented in figure 4.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Mass (amu)</th>
<th>Deviation (ppm)</th>
<th>Resolution</th>
</tr>
</thead>
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<tr>
<td>(Cu^+)</td>
<td>62.9312</td>
<td>26.4</td>
<td>5338</td>
</tr>
<tr>
<td>(CuC_2H_4O_2^+)</td>
<td>122.9550</td>
<td>39.4</td>
<td>4579</td>
</tr>
<tr>
<td>(Cu_2OH^+)</td>
<td>142.8618</td>
<td>2.9</td>
<td>6444</td>
</tr>
<tr>
<td>(C_5H_{11}NCu^+)</td>
<td>148.0183</td>
<td>0.4</td>
<td>6558</td>
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<tr>
<td>(C_5H_{13}NOCu^+)</td>
<td>166.0262</td>
<td>26.4</td>
<td>5338</td>
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</table>

Table 1: Mass fragments associated to copper containing fragments on copper electrodes
Cu⁺ and Cu₂OH⁺ are evenly distributed and their relative presence does not seem to be affected by either the composition or the potentials applied. The large area images for the fragments of interest are presented in the supporting information. On the other hand, the copper complex (\(C_5H_{13}NOCu^+\)) shows a potential dependent behaviour, especially upon the addition of HBDs (figure 4).
Figure 4: Relative intensities of $C_5H_{13}NOCu^+$ a) 1:2 ChCl:EG LW vs 1:2 ChCl:EG HW c) 1:2 ChCl:EG HW vs 1:4 ChCl:EG; and $C_5H_{11}NCu^+$ b) 1:2 ChCl:EG LW vs 1:2 ChCl:EG HW d) 1:2 ChCl:EG HW vs 1:4 ChCl:EG on copper electrodes under varying polarisation potentials.

Figure 4a shows how the increase in $C_5H_{13}NOCu^+$, in 1:2HW, follows the increase in current seen in figure 1 at -0.95V described in the previous section. In the absence of water, 1:2LW, $C_5H_{13}NOCu^+$ is independent of potential and is distributed over the surface. Nevertheless, when water is added to the solvent (1:2HW) the amount of $C_5H_{13}NOCu^+$ becomes dependent on the potential. There is a sudden increase of $C_5H_{13}NOCu^+$ by one order of magnitude when -0.95V is applied, followed by an equal drop when -1.15V is applied. This is caused by water displacing choline at the more negative potential as illustrated in figure 5. This displacement of choline
by water at electrified interfaces has been modelled recently by Mamme et al.\cite{14}. Once choline has been displaced, the breakdown of water further displaces the organic residues through the formation of H$_2$. Meanwhile, figure 4c shows the behaviour $C_5H_{13}NOCu^+$ in 1:2HW and 1:4. Here, 1:2HW has a higher concentration of $C_5H_{13}NOCu^+$ at -0.95V, the potential where the electrolyte decomposition begins, which suggests that this compound is an intermediary step in the decomposition of DES. On the other hand, the 1:4 solution shows a maximum of choline adsorption at -0.60V, the same potential where the limiting current is observed, which matches the data for $C_5H_{13}NOCu^+$. Based on previous studies on the orientation and decomposition of choline during deposition \cite{27, 31}, we show that the passivation of the surface described in them, can be ascribed to not only the formation of choline hydroxide but to the formation of choline metal oxides as well. This trend could seriously limit the application of DES for the deposition of metals that form stable hydroxides\cite{32}.

Figures 4b and d show the behaviour for $C_5H_{11}NCu^+$, a minor product of the dehydration of choline. $C_5H_{11}NCu^+$ in 1:2 LW and 1:2 HW(figure 4b) appears to be independent from both potential and composition. Finally in figure 4d, the effect of excess ethylene glycol is seen, where the amount of $C_5H_{11}NCu^+$ diminishes proportionally to the potential applied. We cannot at the moment suggest a reaction for the further decomposition of $C_5H_{11}NCu^+$.

Ethylene glycol reacts with copper forming $CuC_2H_4O_2^+$. This is consistent with the formation of similar bidentate complexes observed on iron \cite{24}. $CuC_2H_4O_2^+$, is present at much higher proportion than free ethylene gly-
col. In the work of Gu.et.al [23], when ethylene diamine (EDA) is added to ChCl:EG DES the reduction peak shifts to more negative potential, where the EDA is inhibiting the reduction of EG. The observed bidentate complexes are not exclusive to ethylene glycol. As proposed by Mamme. et. al[33] the urea in ChCl:Urea DES reorients itself at the interface so that the amide group is closer to the interface when negative potentials are applied. The mechanism for the formation of these bidentate metal complexes remains to be determined, and the difference in behaviour of N-groups and O-groups needs to be studied further (figure 5).

On the other hand, the formation of the described choline fragments poses an interesting situation. Choline’s charged nitrogen is the part of the molecule that interacts first with the electrode surface according to electrostatic attraction (figure 5) but it is the tail end OH that reacts with copper, leading to the dehydration of the side chain and the formation of $C_5H_{11}NCu^+$. 

Figure 5: Possible choline adsorbates/intermediaries on copper electrodes.
3.2.2. Effect of the applied potential on the decomposition of the electrolyte

In this section, the focus is on the SIMS fragments associated to the solvent. Ethylene glycol can be identified by its molecular fragment $C_2H_5O^+$ with a nominal mass of 61 m/z, but its breakdown fragments are not easily distinguishable from the carbonaceous contamination that is always present on any kind of sample exposed to the atmosphere. On the other hand, choline, which contains nitrogen, can be easily recognised. Fragments associated to a choline residue were found in the mass spectra. The most relevant ones are listed in table 2. A peak found at a nominal mass of 104 m/z was assigned to $C_5H_{14}NO^+$ and represents the molecular fragment of choline. Table 2 shows the mass and resolution of the fragments of interest from the electrolyte.

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Mass (amu)</th>
<th>Deviation (ppm)</th>
<th>Resolution</th>
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</thead>
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<tr>
<td>$C_5H_{14}NO^+$</td>
<td>104.1097</td>
<td>26.4</td>
<td>5338</td>
</tr>
<tr>
<td>$C_2H_5O_2^+$</td>
<td>61.0303</td>
<td>31.1</td>
<td>5708</td>
</tr>
<tr>
<td>$C_3H_8N^+$</td>
<td>58.0680</td>
<td>49.7</td>
<td>4657</td>
</tr>
<tr>
<td>$C_3H_9N^+$</td>
<td>59.0741</td>
<td>19.4</td>
<td>4565</td>
</tr>
<tr>
<td>$C_5H_{12}N^+$</td>
<td>86.1006</td>
<td>48.1</td>
<td>4603</td>
</tr>
</tbody>
</table>

Table 2: Mass fragments associated to a choline and ethylene glycol residue on copper electrodes

The behaviour of the molecular fragment, $C_5H_{14}NO^+$, as a function of potential and composition is analysed in Figure 6. First, at $E_{(OC)}$, 1:2LW and 1:4 show much larger amounts of $C_5H_{14}NO^+$ adsorbed on the surface than 1:2HW. At this point, the affinity between electrolyte and electrode depends
on the solvation and physical properties, such as viscosity. In 1:2LW and 1:4 solutions EG is the main HBD, while in 1:2HW water plays a significant role on the solvation [19, 34]. At -0.60V 1:4 has a significant increase in adsorbed $C_5H_{14}NO^+$ when compared to the other solvents. This corresponds to the limiting current seen in the LSV (figure 1). Since 1:4 is not an eutectic mixture [11, 13], the hydrogen bonding with ethylene glycol doesn’t fully stabilise choline, and the electrochemical decomposition of choline via free radical is ongoing until higher potentials are applied and the decomposition pathway involving the tail OH group takes over. The amount of $C_5H_{14}NO^+$ residue in 1:4 is the lowest for -0.95V and -1.15V.

Figure 6: Relative intensities of $C_5H_{14}NO^+$ as function of potential and composition

Choline is adsorbed on the surface (figure 6) for the 1:2 HW solutions
when the potential applied reach -0.95V [14, 18, 19, 27, 33] as the OH group in choline reacts with the surface. Finally at -1.15V, the intensity of \( C_5H_{14}NO^+ \) drops one order of magnitude in the 1:2HW. This behaviour is consistent with choline hydroxide breakdown caused by the OH\(^-\) formed by the hydrolysis reaction inside the 1:2HW and displacement of choline by water [13, 14]. In the 1:2LW there is a smaller change in the accumulation of \( C_5H_{14}NO^+ \) residue at hydrolysis potentials. The residual water is not enough to displace the choline product, and a inhibiting layer of choline products is formed. The electrochemical behaviours of 1:2LW and 1:2HW are almost identical between -0.95V and -1.15 but have different mechanisms.

On the other hand, \( C_5H_{12}N^+ \), which appeared only as ionisation fragment of \( C_5H_{14}NO^+ \) in previous work [24], increases significantly when water is added to the DES. \( C_5H_{12}N^+ \) is independent from potential and \( C_5H_{14}NO^+ \) in the presence of copper. Figure 7 shows the relation between \( C_5H_{14}NO^+ \) (figure 7a) and \( C_5H_{12}N^+ \) (7b) in 1:2LW and 1:2HW. 7b shows how the \( C_5H_{12}N^+ \) fragment is independent of potential in the presence of water. A similar behaviour can be seen when comparing 1:2HW to 1:4. In figure7c, the presence of molecular fragment \( C_5H_{14}NO^+ \) changes are dependent on the potential applied, but when compared to figure7d, \( C_5H_{12}N^+ \) is independent of potential and one order of magnitude higher than the residue found in 1:2LW. This means that the solvation of choline by the excess HBD, be it water or EG, affects the stability of choline and its decomposition route.
The current reported mechanism for the decomposition of choline ions is based on their behaviour in aqueous media [13]. Choline hydroxide is formed in the presence of OH\(^-\) and then is hydrolysed through a Hoffman elimination, as seen in figure 8. In the Hoffman elimination of choline hydroxide, trimethylamine is the most stable product because it is the least substituted amine [13]. Nevertheless, in this work, the secondary HBDs increase the stability of \(C_5H_{12}N^+\) as final product of the elimination. Figure 8 shows the possible reactions present starting at the formation of choline base (figure 8(1)), followed by the dominant route in the Hoffman elimination (figure...
and finally the minority, or least stable, product of the same reaction (figure 8(3)). The mechanism by which the minority product becomes more stable is still unclear, but based on ethylene glycol and water having the same effect, we propose that it relies on the complexation possible through the excess hydrogen bonds. Regardless of the final product, this information shows that the direct electrochemical decomposition of choline plays a larger role in the breakdown of DES than what had been previously reported by Haerens et al[13]. The increased stability seen in DES baths with high concentration of copper ions [22], can then be explained by a competition between choline and the copper ions for electrons, that favors the metallic ions.

\[ \text{Figure 8: Choline decomposition routes} \]
4. Conclusions

In this work, we have uncovered the effects of excess hydrogen bond donors on the breakdown of choline and their effect on the the interactions with a copper surface. Using ToF-SIMS, we were able to determine the effects of potential on the solvent electrode interactions as presented in figure 9. We have determined that the use excess HBD, whether is water or ethylene glycol, in DES leads to the stabilisation of $C_5H_{12}N^+$. This fragment could be the minority product from the Hoffman elimination or the product of an electrochemical decomposition of choline that starts in the hydroxyl end of the choline. This process is independent from the potential applied to the copper electrode. Additionally, we describe the formation of copper containing compounds ($C_5H_{13}NOCu^+$ and $C_5H_{12}N^+$) as intermediaries in the decomposition of choline in DES with excess hydrogen bond donors. Copper containing intermediates are formed partially through the tail $OH^-$ and reach a maximum at different potentials depending on the HBD used. In the case of water, -0.95V is the potential at which there is maximum accumulation of the residue before water displaces the choline. On the other hand, when ethylene glycol is used the maximum residue is reached at -0.60V, which means that choline can rearrange itself more freely in non eutectic ethylene glycol solutions.
The exact role and effect of these reactions on an electrodeposition process remain to be determined. Many factors play a role during deposition such as the different reactivity of the substrate and deposit with the solvent and the fact that their contributions to the inhibition process can only be determined on pair by pair basis. Additionally, the orientation of the molecules to the surface and their reactions depend on the DES and co-solvent used during the process. [21, 33]. Future work should focus on the influence of metal ion concentration on the residue formation process, as well as the effect of replacing ethylene glycol, for either ethylene diamine or urea.
5. Acknowledgements

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