Deep eutectic solvent (DES) based electrolytes are gaining attention for electrochemical applications. As such, knowledge of the charge transfer kinetics in DES and its dependence on electrolyte composition and temperature is important. Using Cu^{2+} + e⁻ → Cu^{+} as a model system, we demonstrate that metal redox reactions in chloride-containing DES media suffer from sluggish charge transfer kinetics. The exchange current density, \( i_0 \), displayed a peculiar inverse relationship with the bulk chloride concentration, [Cl⁻]. The \( i_0 \) decreased from 7.9 to 3.0 mA/cm² when [Cl⁻] increased from 2.8 to 4.6 M at 30°C. Such dependence is shown to originate from Cl⁻ complexation with reactant and product species. Furthermore, \( i_0 \) increased with an increase in Cu⁺⁺ bulk concentration in the 50–200 mM range. Also, increase in temperature elevated \( i_0 \). The charge transfer coefficient \( \alpha \), however, remained constant (≈0.5) and was unaffected by Cu⁺⁺ or Cl⁻ concentrations or by temperature. To explain how charge transfer kinetics depend on the various system parameters, a model incorporating complexation phenomena was developed and its predictions were compared to experiments.

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Deep eutectic solvent (DES) based electrolytes are gaining attention for energy storage applications. A DES is advantageous over conventional organic and ionic liquid electrolytes because of its low cost, biodegradability, environmental benignity, ease of preparation, non-flammability, non-volatility, and large electrochemical stability window. Ethaline, an eutectic mixture of choline chloride (ChCl) and ethylene glycol (EG) in a 1:2 molar ratio, is a commonly studied DES due to its low viscosity compared to other DESs. Also, the physical properties of ethaline have been comprehensively characterized. Additionally, electrochemical reactions in an ethaline medium have been studied previously using cyclic voltammetry (CV). In the context of electrodeposition, researchers have demonstrated that high current efficiency (>90%) is achievable when electrodepositing Cu from a Cu⁺⁺-containing ethaline electrolyte.

For energy storage applications, such as flow batteries, solution phase redox reactions are preferred over electrodeposition because redox reactions which undergo a soluble-soluble transition are typically reversible, i.e., with fast kinetics, and do not cause electrode ‘shape change’. To investigate ethaline as a potential electrolyte for future redox flow batteries, it is important to study and characterize the kinetics of redox reactions. The Cu^{2+} + e⁻ → Cu^{+} redox reaction, due to its anodic reduction potential, could be used as a redox couple at the battery cathode. Lloyd et al. were among the first to report on the Cu^{2+} + e⁻ → Cu^{+} kinetics in ethaline medium. They reported a cathodic charge transfer coefficient \( \alpha_c \) of 0.2 – 0.3 and a reaction rate constant \( k_0 \) of \((8 – 10) \times 10^{-2}\) cm/s. Their \( \alpha_c \) value suggested an asymmetric current response under cathodic vs. anodic polarization, which stood in contrast to the CV experiments conducted by Abbott et al. Such low \( \alpha_c \) values also contradicted the commonly accepted symmetric (\( \alpha_c \sim 0.5 \)) behavior of the Cu^{2+}/Cu^{+} redox transition in aqueous media. For example, Kiekens et al. reported \( \alpha_c = 0.49 \) and \( k_0 = 4.6 \times 10^{-3}\) cm/s in a chloride-containing aqueous solution. Besides the discrepancy in the charge transfer coefficient, the nearly order of magnitude difference in reaction rate constant between DES and aqueous media was also unexplained. Recently, Shen et al. developed guidelines to accurately measure the kinetics of the Cu^{2+}/Cu^{+} redox transition in ethaline DES. Their measurements yielded an expected symmetric behavior with \( \alpha_c = 0.49 – 0.54 \) and \( k_0 = (1.78 – 1.95) \times 10^{-4}\) cm/s. This was confirmed using three independent techniques – slow scan linear sweep voltammetry (LSV) on Pt RDE, fast scan cyclic voltammetry (CV) on Pt PDE, and slow scan LSV on Pt microelectrode. Consequently, their study established beyond doubt that the Cu²⁺/Cu⁺ redox transition proceeds slowly in DES.

Building on the foundational work by Shen et al., the present contribution aims to investigate further the origins of sluggish kinetics of the Cu²⁺/Cu⁺ redox transition in ethaline with the ultimate goal of revealing the mechanistic underpinnings behind such irreversible behavior. The charge transfer kinetics was measured under a wide variety of experimental conditions to investigate the effect of system variables such as species concentration and temperature on kinetics. New mixtures that deviated from the 1:2 ChCl:EG eutectic composition were formulated and charge transfer kinetics constants in them were measured. It was shown that the kinetics depended on the complexation of Cu⁺⁺ species with chloride. Senanayake and Muri had previously identified that for most aqueous and organic solvents containing excess chloride, the metal ions are stabilized by forming a chloro-complex. In the DES system too, the metal ions tend to form chloro-complexes as shown by EXAFS studies. In the case of Zn electrodeposition, the high chloride activity of the ethaline DES changed the effective concentration of the electroactive Zn species again via complexation. In the present work, we investigate further the complexation of Cu⁺⁺ ions by excess Cl⁻ which is found to be the root cause underlying the sluggish charge transfer kinetics for the Cu²⁺/Cu⁺ redox transition in Cl⁻ rich DES such as ethaline.

**Experimental**

The ethaline-based electrolyte was prepared by mixing choline chloride (ChCl, 99% purity, Acro Organics) and ethylene glycol (EG, anhydrous, 99.8% purity, Sigma-Aldrich) at various molar ratios (ChCl:EG = 1:5, 1:4, 1:3, 1:2) at 80°C until a homogeneous solution was obtained. Cupric chloride dihydrate (CuCl₂·2H₂O, 99% purity, Acros Organics) and cuprous chloride (CuCl, anhydrous, 99% purity, Acros Organics) were then added to provide Cu²⁺ and Cu⁺ concentrations ranging between 50 and 200 mM. In the various electrolytes prepared, the choline chloride from the bare ChCl:EG electrolyte provided base chloride concentrations of 2.5, 2.9, 3.5 and 4.3 M and the addition of Cu⁺⁺ salts at 100 mM concentrations provided an additional
0.3 M Cl⁻. The electrolyte containing CuCl₂·2H₂O was dried at 100°C for 2 hours to reduce the moisture content. The typical moisture content in the various electrolyte mixtures was measured by a Karl Fischer moisture meter to be 3–4 wt%. The water content likely did not affect the Cu²⁺/Cu⁺ redox transition which occurs at potentials within the water electrochemical stability window. The CuCl₂-containing electrolyte was then bubbled with Ar gas to remove dissolved O₂ before CuCl was added. The Ar purge was a preventive measure to remove dissolved O₂ which may oxidize Cu⁺ to Cu²⁺ in the bulk electrolyte. The electrolytes were stored inside an Ar-filled glove box until usage and were used as soon as possible to avoid further moisture and oxygen uptake. Parafilm was used to seal all openings of the electrochemical cell to slow down the moisture and oxygen uptake from ambient during experimentation. For careful analysis, as described in previous work, both Cu²⁺ and Cu⁺ were added to the electrolyte, so that the equilibrium potential of the working electrode was stable and reproducible.

The electrochemical cell consisted of a Pt RDE cell with a water jacket through which warm water was circulated using an Anova water bath to provide the desired electrolyte temperatures of 30, 40, 50 or 70°C. The electrolyte temperature was monitored by a thermometer to ± 0.5°C. During electrochemical experiments, a three–electrode configuration was employed. The working electrode was a 0.5 cm diameter platinum RDE (mirror polished, Pine Research Instrumentation, Inc) with electrode area of 0.196 cm². The RDE rotation was maintained at 1500 RPM by a Pine rotator. The counter electrode was a 0.32 cm diameter graphite rod (Graphite store). The reference electrode was a silver (Ag) wire (99.9% purity, Rio Grande) anodized in ethaline. By holding the Ag wire at a positive potential, a thin, white AgCl layer formed, which provided a pseudo Ag/AgCl reference electrode for experiments. Such reference electrodes have been employed in previous studies of ethaline. All electrochemical measurements were acquired using a Princeton Applied Research PARSTAT-4000 potentiostat. The near steady-state polarization measurements were conducted at a slow scan rate (1 mVs⁻¹) to minimize transient effects. An automated viscometer (RheoSense microVISC) and density meter (DMA 4500 M) took multiple measurements and provided the electrolyte viscosity and density as a function of temperature to the number of significant digits reported below.

**Experimental Determination of Kinetics and Transport Parameters**

**Slow-scan linear sweep voltammetry.**—To experimentally determine the charge transfer kinetics of Cu²⁺/Cu⁺ redox reaction, slow scan linear sweep voltammetry was performed on the Pt RDE in a Cu²⁺ and Cu⁺-containing electrolyte. The electrode potential was scanned from the equilibrium potential to -0.2 V vs. Ag/AgCl at 1 mVs⁻¹. The initial equilibrium potential was established by the concentrations of redox active species, and the slow scan rate ensured the system was under pseudo steady-state conditions. As the electrode potential (E) was scanned, the surface overpotential (ηₛ) at the Pt RDE changed according to

\[ \etaₛ = E - E_{eq} = (V - IR_Ω) - E_{eq} \]  \[ (1) \]

where \( E_{eq} \) is the equilibrium potential, \( V \) is the potential applied by the potentiostat, and \( IR_Ω \) is the ohmic loss due to the electrolyte resistance. The ohmic resistance \( R_Ω \) was measured using electrochemical impedance spectroscopy (EIS) and \( IR_Ω \)-correction was applied as per Eq. 1.

As the surface overpotential increased in the cathodic (\( \etaₛ < 0 \)) direction, the rate of reduction of Cu²⁺ + e⁻ → Cu⁺ increased gradually and eventually reached a mass transport limited plateau at higher overpotentials, as shown by the current response in Fig. 1. The effect of Cu²⁺ and Cu⁺ bulk concentrations on the current response was examined in a 1:2 molar ratio ChCl:EG DES at 30°C (Fig. 1a). The mass transport limited current at high overpotential (\( \etaₛ < -0.4 \) V) was observed to be a function of the Cu²⁺ bulk concentration only. For example, the limiting current doubled when the bulk Cu²⁺ concentration doubled (green, black and red curves), but not when Cu⁺ was doubled (compare black vs. blue curve). On the other hand, the current response at low overpotentials (kinetics dominated regime) depended on both Cu²⁺ and Cu⁺ bulk concentrations. When Cu⁺ concentration doubled, the initial current also increased while tending toward the same limiting current (Fig. 1a, black vs. blue curves).

The effect of temperature on the current response was also examined in a 1:2 molar ratio ChCl:EG electrolyte containing equimolar (100 mM) Cu²⁺ and Cu⁺ (Fig. 1b). As the temperature increased, the rate of Cu²⁺ + e⁻ → Cu⁺ reduction also increased. The mass transport limited current at high overpotential (\( \etaₛ < -0.4 \) V) indicated that the temperature impacted the mass transport parameters. Thus, the diffusion coefficient was carefully measured.

**Determination of Cu²⁺ and Cu⁺ diffusion coefficients.**—The diffusion coefficients were determined from limiting current measurements on a Pt RDE. The electrolyte was kept at constant Cu²⁺ and Cu⁺ concentrations (100 mM), but the total chloride concentration and operating temperature were varied. The chloride concentration (2.8, 3.2, 3.8 or 4.6 M) was modulated by using different molar ratios (1:5, 1:4, 1:3 or 1:2) of the ChCl:EG mixture. The temperature was maintained at 30, 40, 50 or 70°C. Using the Levich equation, the diffusion coefficient was calculated from the anodic and cathodic

![Figure 1. Slow-scan linear sweep voltammetry (1 mVs⁻¹) on a Pt RDE immersed in 1:2 molar ratio ChCl:EG DES. (a) Cu²⁺ concentration controls the diffusion limited current, whereas Cu⁺ only affects the current response at low overpotentials. (b) Operating temperature affects the current response in the kinetics and mass transport limited regions of the polarization curve (Cu²⁺ and Cu⁺ concentrations were 100 mM).](image-url)
Table I. Transport and Kinetic Parameters for Cu$^{2+}$ + e $\rightarrow$ Cu$^{+}$ Redox Transition in ChCl:EG Mixtures.

| ChCl:EG composition and [Cu$^{n+}$]$_b$ | [Cl$^-$] (M) | T (°C) | $\mu$ (cP) | $\rho$ (g/cm$^3$) | $D_{2+} \times 10^{7}$ (cm$^2$/s) | $D_{1+} \times 10^{7}$ (cm$^2$/s) | $i_0$ (mA/cm$^2$) |
|--------------------------------------|-------------|--------|-----------|----------------|-------------------------------|-------------------------------|-----------------|
| 1:5 ChCl:EG                          | 2.8         | 30     | 21.4      | 1.1256         | 4.6                           | 8.2                           | 7.9             |
| 100 mM Cu$^{2+}$                     | 40          | 15.1   | 1.1193    | 6.9            | 12.0                          | 11.8                          |
| 100 mM Cu$^{1+}$                     | 50          | 11.4   | 1.1130    | 9.5            | 16.0                          | 17.4                          |
|                                      | 70          | 7.3    | 1.1003    | 18.1           | 28.2                          | 23.0                          |
| 1:4 ChCl:EG                          | 3.2         | 30     | 23.7      | 1.1272         | 4.6                           | 8.1                           | 6.6             |
| 100 mM Cu$^{2+}$                     | 40          | 16.8   | 1.1209    | 6.6            | 11.3                          | 10.1                          |
| 100 mM Cu$^{1+}$                     | 50          | 12.5   | 1.1147    | 9.0            | 15.1                          | 12.3                          |
|                                      | 70          | 7.8    | 1.1023    | 16.8           | 26.2                          | 18.2                          |
| 1:3 ChCl:EG                          | 3.8         | 30     | 26.0      | 1.1277         | 3.8                           | 6.5                           | 5.0             |
| 100 mM Cu$^{2+}$                     | 40          | 18.2   | 1.1217    | 5.5            | 9.2                           | 7.1                           |
| 100 mM Cu$^{1+}$                     | 50          | 13.5   | 1.1157    | 7.5            | 12.2                          | 8.7                           |
|                                      | 70          | 8.6    | 1.1036    | 13.9           | 21.5                          | 15.1                          |
| 1:2 ChCl:EG                          | 4.6         | 30     | 36.3      | 1.1278         | 2.6                           | 4.6                           | 3.0             |
| 100 mM Cu$^{2+}$                     | 40          | 24.9   | 1.1220    | 3.9            | 6.8                           | 4.4                           |
| 100 mM Cu$^{1+}$                     | 50          | 18.2   | 1.1162    | 5.4            | 9.5                           | 5.6                           |
|                                      | 70          | 11.1   | 1.1047    | 10.4           | 17.9                          | 9.5                           |
| 1:1 ChCl:EG                          |              | 30     |           |                |                               |                               | 1.0             |
| 50 mM Cu$^{2+}$                      |              |        |           |                |                               |                               | 2.0             |
| 1:2 ChCl:EG                          |              | 30     |           |                |                               |                               | 2.5             |
| 100 mM Cu$^{2+}$                     |              |        |           |                |                               |                               | 4.3             |
| 50 mM Cu$^{1+}$                      |              |        |           |                |                               |                               | 4.3             |
| 1:4 ChCl:EG                          |              |        |           |                |                               |                               | 4.3             |
| 100 mM Cu$^{1+}$                     |              |        |           |                |                               |                               | 4.3             |

$T$ = temperature; $\mu$ = viscosity; $\rho$ = density; $D_{2+}$ = Cu$^{2+}$ diffusion coefficient, $D_{1+}$ = Cu$^{1+}$ diffusion coefficient, $i_0$ = exchange current density

Limiting currents:

$$i_L = -0.62nF\frac{D_{2+}^{\frac{1}{2}}}{\rho} \left[ \frac{\mu}{\rho} \right]^{\frac{1}{2}} [Cu^{2+}]_b \omega^{\frac{2}{3}}$$  \[2\]

$$i_L = 0.62nF\frac{D_{1+}^{\frac{1}{2}}}{\rho} \left[ \frac{\mu}{\rho} \right]^{\frac{1}{2}} [Cu^{1+}]_b \omega^{\frac{1}{3}}$$  \[3\]

where $i_L$ is the limiting current density (superscript ‘c’ and ‘a’ denote cathodic and anodic reactions, respectively), $n$ is the number of electrons transferred, $F$ is the Faraday’s constant, $D_{2+}$ and $D_{1+}$ are the diffusion coefficients, $\mu$ is the viscosity of the electrolyte, $\rho$ is the density, $[Cu^{2+}]_b$ and $[Cu^{1+}]_b$ are the concentrations in the bulk electrolyte, and $\omega$ is the RDE rotation speed. Because the viscosity and density of the electrolyte are a function of the electrolyte composition and temperature, both were carefully measured using a viscometer and density meter up to 50°C. The data point for 70°C was extrapolated using the Vogel-Fulcher-Tamman (VFT) model for viscosity and linear regression for density, as has been done previously in literature. The viscosity was found to depend on the moisture content. Therefore, efforts were taken to maintain the same moisture content (3-4 wt%) across all samples. The viscosity and density values agree with literature measurements and are listed in Table I.

The cathodic and anodic limiting currents were measured at RDE rotation speeds ranging from 500 to 1500 RPM. A linear relationship between $i_L$ and $\omega^{\frac{1}{2}}$ was confirmed, indicating Levich behavior. The application of the Levich equation to extract diffusion coefficients was discussed in detail in our previous work. The same technique was applied here, and the measured diffusion coefficients at various chloride concentrations and temperatures are listed in Table I. It is noteworthy that the diffusion coefficients reported in Table I are those of the respective chloro-complexes of Cu$^{1+}$ and Cu$^{2+}$. In general, the diffusion coefficients of the chloro-complexes decreased with increasing chloride concentration (Fig. 2) at any given temperature. This decrease is due to an increase in the electrolyte viscosity as more ChCl was added to the electrolyte to raise the chloride concentration. With increasing temperature, the diffusion coefficients of the Cu$^{2+}$-complexes were observed to increase (Fig. 2). As tabulated in Table I, the viscosity of the electrolyte decreased at higher temperatures thereby resulting in faster species diffusion.

To investigate the relationship between diffusion coefficients and electrolyte viscosity, the $D_{2+}$ and $D_{1+}$ values were plotted as a function of viscosity regardless of chloride concentration or temperature (Fig. 3a). The diffusion coefficients exhibited a strong linear dependence on the inverse of viscosity (Fig. 3b), which suggests Stokes-Einstein behavior. The Stokes-Einstein equation describes the diffusion of a spherical object with radius $r$ as it moves through a medium with viscosity $\mu$ at temperature $T$.

$$D = \frac{k_B T}{6\nu r^2}$$  \[4\]

By applying this equation, the Cu$^{2+}$-Cl$_n$ complex was estimated to have a solvation sphere of 2.2 Å in radius. The Cu$^{1+}$-Cl$_n$ complex solvation sphere was 1.3 Å in radius. The constant sizes of the solvation spheres of the chloro-complex of Cu$^{1+}$ and Cu$^{2+}$ indicate that the coordination number is relatively unaffected in the range of experimental parameters studied and that the key modulator of diffusivity is the electrolyte viscosity.

**Determination of Cu$^{2+}$ + e $\rightarrow$ Cu$^{+}$ reduction kinetics.—** To measure the charge transfer kinetics of the Cu$^{2+}$ + e $\rightarrow$ Cu$^{+}$ reduction reaction, slow scan (1 mV/s) linear sweep voltammetry was deployed on the Pt RDE immersed in the various ChCl:EG mixtures. The Cu$^{2+}$ concentration, chloride concentration and operating temperature were varied systematically within the ranges described above. The surface overpotential at the electrode was scanned in the cathodic direction.
and the current response was measured, then analyzed by applying the Tafel equation:

\[
i = i_0 \left(1 - \frac{i}{i_0}\right) \exp\left(-\frac{\alpha_c F}{RT} \eta_s\right)
\]

where \(i_0\) is the exchange current density, \(\alpha_c\) is the cathodic charge transfer coefficient, and all other variables have their usual meanings. As expected, the current reached a limiting current plateau at large overpotentials and its value corresponded to the reported diffusion coefficients (Table I). At moderate overpotentials, the Tafel equation could be fitted to the polarization data, as shown in Fig. 4a.

While the measured current response depended on the Cu\(^{2+}\), Cu\(^{1+}\) and Cl\(^-\) concentrations (Fig. 4b), the Tafel slope obtained remained constant providing a relatively unchanged value of the charge transfer coefficient \(\alpha_c\) of \(\sim 0.5\) (indicating symmetric behavior in cathodic and anodic polarization). In addition, the charge transfer coefficient remained \(\sim 0.5\) for various compositions of the ChCl:EG mixture as well as over the entire operating temperature range studied (Fig. 5).

From the Y-intercept of the Tafel plots (Fig. 4), the exchange current density was extracted (Table I). According to the classical Butler-Volmer theory, the exchange current density can be expressed as:

\[
i_0 = nF k_0 [\text{Cu}^{2+}]^{1-\alpha_c} [\text{Cu}^{1+}]^{\alpha_c}
\]

where \(k_0\) is the reaction rate constant. Assuming \(\alpha_c = 0.5\), \(i_0\) is expected to increase in proportion to \(([\text{Cu}^{2+}] / [\text{Cu}^{1+}])^{0.5}\). This linear proportionality could be clearly observed in a 1:2 ChCl:EG DES at 30°C (Fig. 6a). From the slope, the reaction rate constant was calculated as \(k_0 = 2.4 \times 10^{-4} \text{ cm/s}\), which is in reasonable agreement with our previous report.

The observed reaction rate constant \((k_0 = 2.4 \times 10^{-4} \text{ cm/s})\) in 1:2 ChCl:EG DES at 30°C is much lower than that reported for the same reaction in an aqueous medium. Kiekens et al. using aqueous electrolytes reported \(\alpha_c = 0.49\) and \(k_0 = 46 \times 10^{-4} \text{ cm/s}\) for the Cu\(^{2+}\) + e \(\rightarrow\) Cu\(^{1+}\) reduction reaction. The sluggish kinetics in DES is likely not due to surface adsorbed species of chloride because of their presence in large excess (>1 M) in the electrolyte. In such excess concentration and in the potential region of Cu\(^{2+}/Cu^{1+}\) redox transition, the electrode surface will experience nearly saturated Cl\(^-\) coverage and not one which gradually increases with bulk Cl\(^-\) concentration to produce a monotonically decreasing exchange current density as in Fig. 6. Besides adsorption, solvation is also not the likely cause for the observed sluggish kinetics. Halley et al. reported that Cu\(^{2+}/Cu^{1+}\) redox transition in an aqueous solution is not dominated by solvent rearrangement, but by the energetics of solvated species approaching the electrode surface. We believe that such effects are not dominant in our DES system because when we compared voltammetry response on a glassy carbon (GC) RDE to that on a Pt RDE (see supplemental information), the kinetics of the Cu\(^{2+}/Cu^{1+}\) reaction were measurably different. The dependence of kinetics on the substrate suggests that solvent effects (like reorientation) are likely not the rate determining factors.
It is known that metal ions, such as Cu$^{2+}$ and Cu$^{+}$, form metal chloride complexes in aqueous solutions with high chloride content. Abbott et al. showed that the Cu speciation in a ChCl:EG DES displayed similar UV-Vis spectrum as in an 8 M LiCl aqueous solution. They further determined that the Cu(II) tetrachloro complex, CuCl$_4^{2-}$, is the predominant species for Cu$^{2+}$, and CuCl$_2^-$ is the predominant form of Cu$^{+}$ although lower order complexes are present in tandem. Therefore, the higher order CuCl$_n$ complexes could stabilize the Cu$^{n+}$ and impede its participation in electron transfer reactions whereas the less stable (less coordinated) species may be available to participate in reactions.

As the ChCl:EG ratio shifted from 1:5 to 1:2, the total chloride concentration in the electrolyte increased from 2.8 M to 4.6 M. The exchange current density as a function of the total chloride concentration is plotted in Fig. 6b. The kinetics became more sluggish when the chloride concentration increased. This supports the role of chloro-complex formation mentioned in the preceding paragraph. From aqueous Cu speciation data, Cu ions form CuCl$_n$ complexes at high chloride concentrations. As the chloride concentration increases (> 1 M), the complex shifts to higher order species ($n = 4$). The same is known about Cu speciation in DES. Thus, as the chloride concentration increases, we would expect a reduced number of ‘free’ Cu ions (i.e., lower concentration of weakly coordinated Cu$^{n+}$) to be available for direct electrochemical reaction. A consequence of this effect would be a decrease in the exchange current density ($i_0$) value per Eq. 6.

Note that this dependence of kinetics on ‘free’ or loosely coordinated Cu$^{n+}$ is distinct from the system behavior when under diffusion limitations. Under mass transport control, the electroactive species near the electrode surface are exhausted. While more electroactive species may be brought to the electrode surface via diffusion, the higher order complexes of Cu$^{n+}$ near the electrode can also gradually generate the ‘free’ electroactive species by dissociation whereby they (higher order complexes) too develop a diffusion-limited concentration gradient. A net result of all this is a depletion of the total Cu species concentration in the boundary layer thus explaining why mass transport limitations are sensitive to the total Cu$^{n+}$ concentration.

By varying the operating temperature, its effect on charge transfer kinetics could be studied. The exchange current density is directly proportional to the operating temperature (Fig. 6b). This dependence, together with the dependence of $i_0$ on the Cu$^{n+}$ and chloride concentration, is analyzed in the modeling section below.

### Mathematical Modeling of Complexation Effects on Reaction Kinetics

**Model setup and comparison to experimental results.**—To evaluate the effects of complexation on exchange current density, a mathematical model was formulated. The model is based on the assumption that Cu$^{n+}$ ions form chloro-complexes in ChCl:EG mixtures. The
electroactive chloro-complexes assumed are Cu(II)Clₘ and Cu(I)Clₘ where \( n \) and \( m \) represents the number of Cl⁻ needed to complex Cu²⁺ and Cu⁺, respectively. We assume that Cu(II)Clₘ and Cu(I)Clₘ are in equilibrium with higher order Cl⁻ complexes as shown in Eqs. 7 and 8. Previous studies by Hartley et al. indicated that CuClₙ and CuCl₂ are the predominant higher order complexes in 1:2 molar ratio ChCl:EG DES, however, we develop here a generalized model in which the value of \( n \) and \( m \) although fixed are a priori unknown:

\[
\text{CuCl}_n^{2-} + x\text{Cl}^- \rightleftharpoons \text{CuCl}_{n+x}^{2-} \quad [7] \\
\text{CuCl}_m^{1-} + y\text{Cl}^- \rightleftharpoons \text{CuCl}_{m+y}^{1-} \quad [8] \\
\text{CuCl}_n^{2-} + e^- \rightleftharpoons \text{CuCl}_m^{1-} \quad [9]
\]

where CuClₙ⁻² and CuClₘ⁻¹ are the higher order complexes for Cu²⁺ and Cu⁺ and CuClₙ⁻² and CuClₘ⁻¹ are the lower order electroactive complexes involved in the charge transfer reaction Eq. 9. For simplicity, Eq. 9 assumes no involvement of free chloride \((m = n)\). Thus, the exchange current density from classical Butler-Volmer theory (Eq. 6) can now be written as:

\[
i_0 = nFk_0\left[\text{CuCl}_n^{2-}\right]^{1-\alpha_c}\left[\text{CuCl}_m^{1-}\right]^{\alpha_c} \quad [10]
\]

Since the concentrations of CuClₙ⁻² and CuClₘ⁻¹ are not known a priori, we involve the equilibrium constants \(K_{2+}\) and \(K_1^+\) of Reactions 7 and 8 above:

\[
K_{2+} = \frac{[\text{CuCl}_{n+1}^{2-}]}{[\text{CuCl}_n^{2-}][\text{Cl}^-]} \quad [11] \\
K_1^+ = \frac{[\text{CuCl}_{m+1}^{1-}]}{[\text{CuCl}_m^{1-}][\text{Cl}^-]} \quad [12]
\]

Additionally, since the total Cu²⁺ and Cl⁻ is fixed, \([\text{Cu}^{2+}]_{\text{total}}, [\text{Cu}^+_{\text{total}}]\) and \([\text{Cl}^-]_{\text{total}}\) are known quantities. Mass balance on the species then provides:

\[
1 \times [\text{CuCl}_n^{2-}] + 1 \times [\text{CuCl}_{n+m}^{2-}] = [\text{Cu}^{2+}]_{\text{total}} \quad [13] \\
1 \times [\text{CuCl}_m^{1-}] + 1 \times [\text{CuCl}_{m+y}^{1-}] = [\text{Cu}^+]_{\text{total}} \quad [14] \\
n \times [\text{CuCl}_n^{2-}] + (n+x) \times [\text{CuCl}_{n+m}^{2-}] + m \times [\text{CuCl}_m^{1-}] + (m+y) \times [\text{CuCl}_{m+y}^{1-}] + [\text{Cl}^-] = [\text{Cl}^-]_{\text{total}} \quad [15]
\]

Because our experiments are done under conditions of excess chloride and [Cu⁺]_{total} \(\ll\) [Cl⁻]_{total}, we can assume that most of the bulk chloride is ‘free’, simplifying Eq. 15 to

\[
[\text{Cl}^-] \approx [\text{Cl}^-]_{\text{total}} \quad [16]
\]

Eqs. 11–16 combined with Eq. 10 yields

\[
i_0 = nFk_0\left(\frac{[\text{Cu}^{2+}]_{\text{total}}}{1 + [\text{Cl}^-]_{\text{total}}^{1-\alpha_c}}\right)^{1-\alpha_c}\left(\frac{[\text{Cu}^+]_{\text{total}}}{1 + [\text{Cl}^-]_{\text{total}}^{\alpha_c}}\right)^{\alpha_c} \quad [17]
\]

As shown by our experiments (Fig. 5) above, the charge transfer coefficient \(\alpha_c\) remains \(\sim 0.5\) under conditions studied herein. Eq. 17 can hence be written as

\[
i_0 = nFk_0\left([\text{Cu}^{2+}]_{\text{total}}[\text{Cu}^+]_{\text{total}}^{0.5}\right)^{0.5} \quad [18]
\]

The model (Eq. 18) predicts the exchange current density dependencies on system parameters that are in good qualitative agreement with the experimental observations reported in Fig. 6:

a. Eq. 18 shows that the exchange current density is expected to be a linear function of the square root of the product of the Cu⁺⁺ species concentration \(i_0 \propto ([\text{Cu}^{2+}]_{\text{total}}[\text{Cu}^+]_{\text{total}})^{0.5}\) which is consistent with Fig. 6a data.

b. As the total chloride concentration [Cl⁻]_{total} increased in Fig. 6b, \(i_0\) decreased. This again is consistent with the inverse dependence of \(i_0\) on [Cl⁻]_{total} in Eq. 18.

c. The equilibrium constants \(K_{2+}\) and \(K_1^+\) are temperature dependent. Meng and Bard reported that, as the temperature shifted higher, a lower coordination number was favored by the Cu²⁺–Cl⁻ complex in aqueous media.5 Hartley suggested that the \(K\) values are different in DES than in aqueous media, hence no quantitative analysis can be done unless \(K\) values are experimentally measured in DES. However, a qualitative assessment is still possible and useful. The equilibrium constants depend on the enthalpy of formation. For some chloro-complexes, such as CuCl₂ and CuCl, available data suggests that complex formation is exothermic. As temperature increases, the equilibrium in Eqs. 7 and 8 is expected to shift to the left, i.e., higher order complexation is retarded. This would imply that the concentration of the weakly coordinated, i.e., electroactive, Cu⁺⁺ species would be higher at elevated temperatures, thus explaining the increase in the exchange current density per Eq. 10. Additionally, temperature may also directly affect \(i_0\) in Eq. 10. All this supports the experimental observation that charge transfer kinetics will be accelerated at elevated temperatures (consistent with Fig. 6b data).

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Figure 6. (a) The exchange current density measured on a Pt RDE in 1:2 molar ratio ChCl:EG DES at 30°C was linearly dependent on the square root of the product of the Cu⁺⁺ species concentrations. The dashed line represents the best fit line. (b) In equimolar (100 mM) Cu²⁺ and Cu⁺ containing ChCl:EG mixtures, the exchange current decreased with increasing Cl⁻ concentrations but it increased with increasing temperature.
Conclusions

In this work, the charge transfer kinetics of the Cu^{2+} + e ↔ Cu^{1+} redox transition was analyzed in a chloride-containing ChCl:EG deep eutectic solvent. The charge transfer coefficient (α) and the exchange current density (i_0), as well as the mass transport parameters (D_0 and D_1) were precisely measured as a function of species concentrations and temperature. Upon analysis, the charge transfer kinetics were found to be sluggish as indicated by an order of magnitude lower i_0 in the chosen DES than that known for the same reaction in aqueous media. The dependence of i_0 on the Cu^{2+} concentration, Cl\textsuperscript{-} concentration and temperature pointed toward the role of complexation, i.e., Cu^{1+} and Cu^{2+} undergoes complexation with Cl\textsuperscript{-} whereby the lower coordination number species (least complexed with Cl\textsuperscript{-}) are available for participating in charge transfer reactions. Invoking arguments of equilibrium in a simple mathematical model, it was shown that this complexation effect explains qualitatively the key dependencies observed in experimental kinetics data. Our findings will guide future experimental work on prevention or circumvention of complexation leading potentially to identification of reversible redox chemistries in DES media.

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