

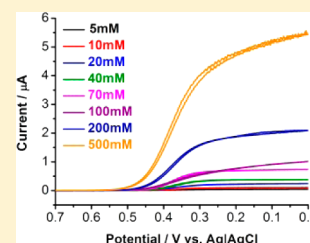
Electrochemistry of High Concentration Copper Chloride Complexes

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ABSTRACT: High concentrations of copper chloride solutions (in the molar range) are used in several industrial applications. In this work, we investigated the species distribution of copper chloride complexes and how to measure the copper concentration precisely at high concentrations using electrochemical methods, by including migrational effects. The latter, in fact, can be useful in determining the nature of the species in solution undergoing electron transfer at the electrode. The study indicates that the main species of Cu(II) complexes in high chloride concentration is CuCl_4^{2-} and the main species of Cu(I) complexes are CuCl_2^- and CuCl_3^{2-} . However insoluble CuCl is an intermediate in the process and can deactivate the electrode surface. This can be ameliorated by increasing the temperature or Cl^- concentration.

Under these conditions, voltammetry with an ultramicroelectrode (UME) can measure copper concentration with good precision even at 1 M Cu(II) concentrations in a few molar chloride. The main charge of the species can be determined by fitting to a migration model.



Molar concentrations of copper solutions are used in industrial processes, such as the HydroCopper process for recovery of copper from chalcopyrite concentrates and might also be applied to flow battery applications. Measuring high concentrations of copper complexes accurately and understanding their electrochemistry is thus important. In this work, we discuss the electrochemistry of such solutions as related to smaller concentrations and describe how to determine the copper concentration over a wide range using voltammetric techniques.

Copper chloride complexes have been well-studied electrochemically.^{1–7} Coordination by chloride ions stabilize the Cu(I) species so that stepwise reduction to Cu(I) and then to Cu(0) is observed, rather than the direct two-electron-transfer reduction to Cu(0), as seen, for example, in sulfate or nitrate solutions. In these studies, the voltammetric behavior of millimolar levels of Cu(II) to Cu(I) reduction in the chloride environment was governed by diffusion, and the voltammograms agree with our low concentration study in this paper. However, despite the large number of electrochemical studies of copper chloride systems, an understanding of the voltammetry and determination of the 0.1 M to molar range of copper concentrations in chloride solution have not been described.

A frequent method of measuring such high concentrations of copper in chloride solutions is based on a potentiometric method, i.e., measuring the redox potential, e.g., with a digital multimeter.^{1,2} This method is quick and simple. However, potentiometric methods at molar concentrations are not precise and using the redox potential to find the concentration is not straightforward. Both cupric and cuprous chloride complexes have several forms,^{8–15} for Cu(II) there are at least five species: Cu^{2+} , CuCl^+ , CuCl_2 , CuCl_3^- , and CuCl_4^{2-} . The distribution of the complexes depends strongly on the free chloride concentration. For Cu(I), there are at least six complexes:

Cu^+ , CuCl , CuCl_2^- , CuCl_3^{2-} , $\text{Cu}_2\text{Cl}_4^{2-}$, and $\text{Cu}_3\text{Cl}_6^{3-}$; because of the presence of polynuclear Cu species, the ratio of the complexes depends on both the concentration of copper ion and free chloride. Since each pair of cupric/cuprous chloride complexes have a unique redox potential, the overall redox potential of Cu(II)/Cu(I), assuming equilibration, is the weighted average of all redox pairs. The studies described here were carried out at high chloride concentrations where the most coordinated forms predominate.

Cyclic voltammetry is a useful technique for measuring the concentration of electroactive species.¹⁶ There has been little work done, however, on measuring high concentrations (e.g., >50 mM) with traditional macroelectrodes, because the large faradic currents produce large resistive (iR) drops that seriously distort the voltammograms and affect the measured currents. The advent of ultramicroelectrodes (UMEs) with micrometer-dimension electrodes, much smaller currents flow, even with M concentrations, so measurements of high concentrations should be possible. However, an important consideration even with UMEs is the migration effect, where mass transfer from the electric field must be considered. In most electrochemical studies, the analyte concentration is much lower than the concentration of supporting electrolyte, so that only diffusion is considered as the mass transfer mechanism. In systems where molar levels of copper chloride solutions are used, the supporting electrolyte cannot be made sufficiently high that diffusion is the only form of mass transfer. In such cases, migration must be considered. Usually migration is studied with millimolar concentrations of the electroactive species by limiting the amount of supporting electrolyte.^{17–20} In this work, we probe the effect of migration in both low supporting

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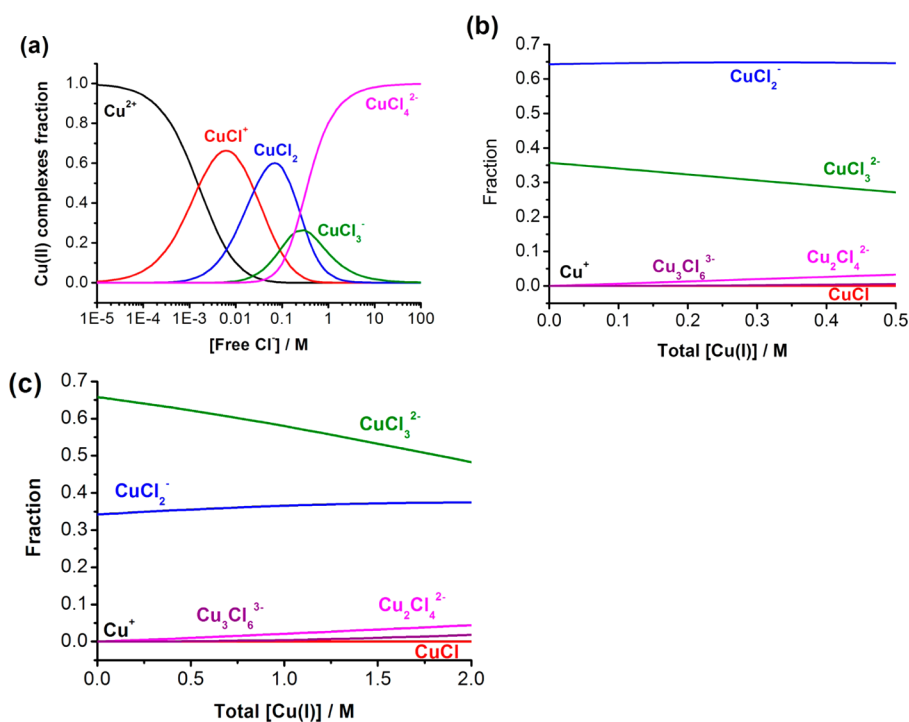


Figure 1. (a) Fraction of cupric chloride complexes vs free chloride concentration; (b) fraction of cuprous chloride complexes vs total Cu(I) in solution 1, 2.5 M NaCl plus 0.1 M HCl; (c) fraction of cuprous chloride complexes vs total Cu(I) in solution 2, 9 M LiCl.

electrolyte and high analyte concentration experimentally and by simulation. As we demonstrate, the presence and treatment of migration is useful in determining speciation, i.e., the charge on the predominant species.

EXPERIMENTAL SECTION

Chemicals. All chemical were reagent grade from Fisher Scientific and used without further purification.

Instrumentation. The scanning electrochemical microscopy (SECM) measurements were carried out on a CH Instruments (Austin, TX) model CHI920. The cyclic voltammetry (CV) was carried out either on a Bioanalytical Systems (BAS) model 100A (Bioanalytical System, Inc., West Lafayette, IN), a model CHI660 workstation, or a CHI920. A three electrode system was used with a platinum wire counter electrode and a Ag|AgCl reference electrode (CHI111).

The scanning electron microscopy (SEM) images were taken by a Quanta 650 instrument. The X-ray photoelectron spectroscopy (XPS) spectra were acquired with a Kratos Axis Ultra X-ray photoelectron spectrometer.

Electrodes. Platinum wire (25 μm , Goodfellow Cambridge Limited) was used to fabricate the UMEs for CV and the SECM tips by procedures described elsewhere.²¹ Briefly, a glass capillary (1.5 mm, Fisher Scientific) was sealed using a torch to produce a narrow cavity in the end. The platinum wire was placed in the narrow cavity. The glass was then heated slowly under vacuum to seal the platinum wire. The end of the platinum wire was attached to a copper wire with silver epoxy to provide connection. For SECM experiments, the end of the electrode was polished to a cone shape with an RG value (the ratio of the glass diameter to the UME metal disk diameter) value of about 2.

Simulations. A numerical model was developed using Comsol 3.5a, coupling diffusion and migration for electro-

chemical measurements. The details of this model are described elsewhere.²²

RESULTS AND DISCUSSION

Distribution of Copper Complexes. The distribution of Cu(II) and Cu(I) chloride complexes in aqueous solution as a function of free chloride was calculated from stepwise (K_n) and overall (β_n) stability constant values from Sillen and Martell (Figure 1a).²³ Since Cu(II) in chloride forms only mononuclear complexes, the distribution of the complexes only depends on the free chloride concentration but not on the total Cu(II) concentration or the total chloride concentration. At free chloride concentration above about 1 M, the CuCl₄²⁻ species predominates, along with small amounts of CuCl₃⁻ and a very small amount of CuCl₂.

In Cu(I) solutions with free chloride, the distribution of the cuprous chloride complexes depends on both the free chloride concentration as well as the total Cu(I) concentration (Figure 1b,c) (cuprous chloride species vs concentration of total Cu(I), with (solution 1) 2.5 M NaCl and 0.1 M HCl or (solution 2) 9 M LiCl, the two main conditions used in this study. With chloride solution 1, the main Cu(I) species are CuCl₂⁻ and CuCl₃²⁻ with a ratio of about 2:1. However with solution 2, the fraction of CuCl₃²⁻ is higher than that of CuCl₂⁻. In both parts b and c of Figure 1, the Cu(I) concentration was only calculated up to the solubility limits; no CuCl(s) was considered.

In high concentration of cuprous chloride or cupric chloride with a high concentration of NaCl and HCl, knowledge of the activity coefficients would be useful in obtaining more accurate estimations of concentrations. However experimental activity coefficients of the species of interest under the experimental conditions of interest are not available and theoretical predictions, e.g., by Debye–Huckel²⁴ or Pitzer theory²⁵ do not provide accurate predictions at very high ionic strengths

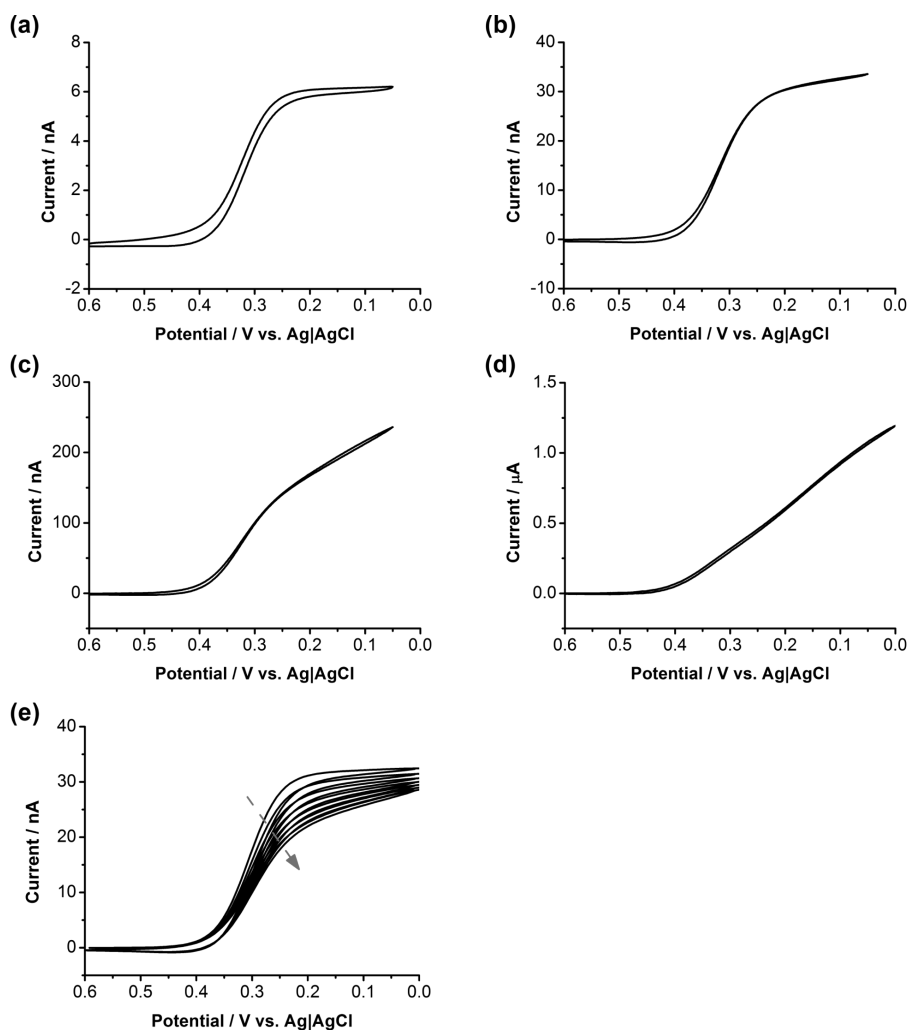


Figure 2. Cyclic voltammograms of different concentrations of cupric chloride in 2.5 M NaCl with 1% HCl, using a 25 μm platinum microelectrode at a scan rate of 10 mV/s: (a) 2 mM, (b) 10 mM, (c) 0.1 M, (d) 0.5 M, and (e) 10 mM at multiple scans; gray arrow indicates the initial scan to last scan.

and in mixed electrolytes. However, because activity coefficients tend to increase at higher ionic strengths (after the initial decrease), the corrections from the concentration or low ionic strength value is somewhat mitigated.²⁶ Moreover we are mainly interested here in the nature of the species with excess free chloride, which is less sensitive to small changes in the formal equilibrium constant.

In most experiments involving copper chloride, the total chloride concentration can be obtained directly while the free chloride concentration requires an equilibrium calculation based on material and charge balance and the stability constants.

High Concentration Cupric Chloride in 2.5 M NaCl and 0.1 M HCl Solution: Surface Precipitation Effects. At high concentrations of Cu(II), high ohmic drops limit the use of macroelectrodes. Therefore, the voltammetry of cupric chloride was studied with a 25 μm platinum UME over a wide range of concentrations with different concentrations of supporting electrolyte.

In the first set of experiments, the supporting electrolyte was fixed at 2.5 M NaCl with 1% HCl (0.12 M), in addition to the added CuCl₂. CuCl₂ of 2 mM, 10 mM, 0.1 M, and 0.5 M was tested. While the 2 mM and 10 mM CuCl₂ voltammograms showed typical diffusion controlled current, the 0.1 M CuCl₂

did not show a limiting current. Instead, there was a slow increase in reduction current after 0.25 V. The 0.5 M CuCl₂ only showed a constant increase. This behavior may be due to several factors: migration at the high ratio of analyte to supporting electrolyte; surface precipitation of CuCl; speciation ratio changes among CuCl⁺, CuCl₂, CuCl₃⁻, and CuCl₄²⁻ when the free Cl⁻ concentration changes at the electrode surface during reduction; or pH change near the electrode surface. However, during multiple scans of 10 mM CuCl₂ solution, the shape of the voltammetric curve at a UME gradually changed (Figure 2e). The fact that the original curve was restored, if the electrode surface was repolished, indicates that surface precipitation with some electrode passivation was the cause of the voltammetry changes. Similar behavior was observed with higher Cu(II) concentrations but not with 2 mM CuCl₂. Since CuCl is known to have limited solubility, compared to the other Cu species, this was the best candidate for precipitation on the electrode surface.

SEM–energy dispersive X-ray (EDX) and XPS experiments were carried out to identify the composition of the precipitate. To obtain a sample, 0.05 V (where Cu(II) is reduced to Cu(I)) was applied to 25 μm platinum wire or foil for 100 s in 0.5 M CuCl₂ in 2.5 M NaCl. The Pt wire- or foil was briefly rinsed in

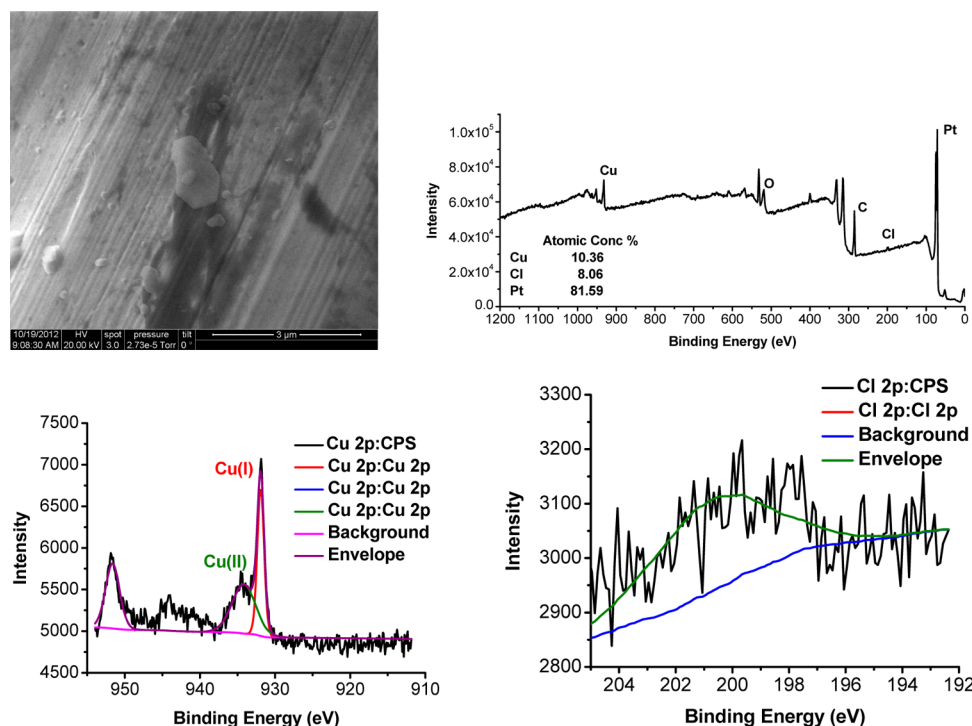


Figure 3. (top left) SEM image of precipitation on 25 μm platinum wire; (top right) XPS data of precipitation on platinum foil; (bottom left) XPS data of copper oxidation state in the precipitation on platinum foil; (bottom right) XPS data of chloride in the precipitation on platinum foil.

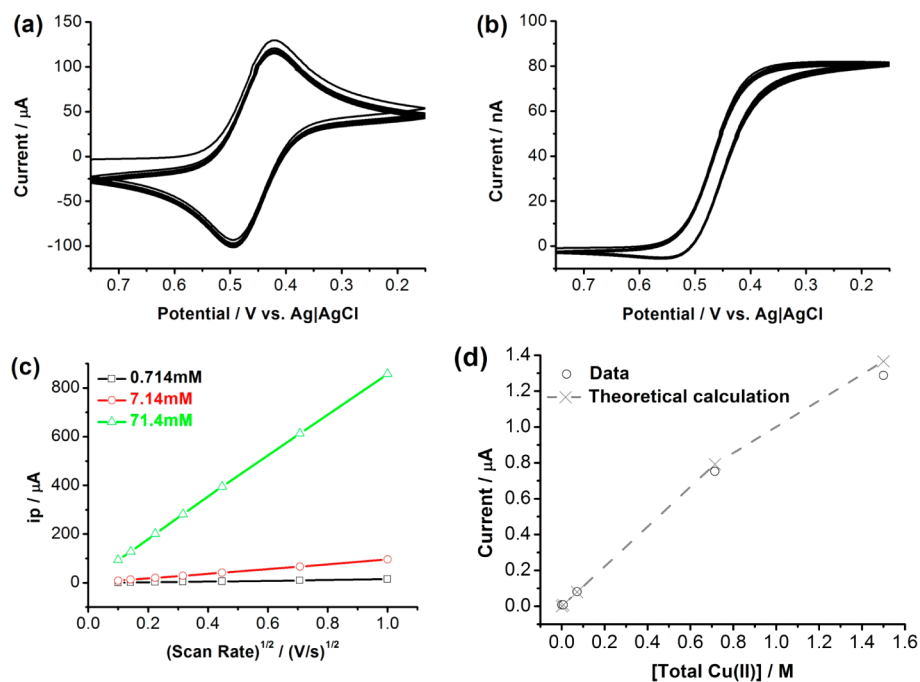


Figure 4. Multiple cyclic voltammograms of 71.4 mM CuCl_2 in 9 M LiCl , at scan rate of 20 mV/s: (a) 2 mm platinum macroelectrode for 60 min; (b) 25 μm platinum microelectrode for 60 min; (c) peak current vs the square root of scan rate at 2 mm platinum; (d) limiting current vs concentration with a 25 μm platinum UME.

deoxygenated deionized water and kept under argon environment until the EDX and XPS analysis.

By SEM, the Pt wire showed small islands of precipitate (Figure 3, top left). EDX showed that these islands were mainly Cu and chloride, with some O and C contamination. The Pt foil showed similar precipitates, showed mainly Cu(I) and chloride by XPS. The ratio of the copper to chloride was about

1:1, which suggested CuCl as the precipitate. The small amount of the Cu(II) probably arises from some Cu(I) oxidation by O_2 in air,²⁷ as the platinum wire and foil were briefly exposed to air during transfer.

High Concentration Cu(II) in 9 M LiCl : Migration Effect on Reduction of Negatively Charged Cu(II) Species. Because fouling of the electrode during reduction of high

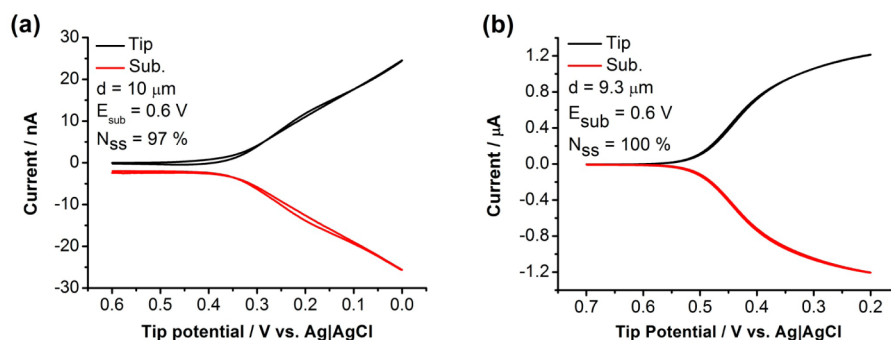


Figure 5. SECM of copper chloride in tip generation-substrate collection mode. Both tip and substrate electrodes were of platinum, 25 and 100 μm , respectively: (a) 10 mM copper chloride in 2.5 M NaCl and 1% HCl solution, collection efficiency = 97%; (b) 0.714 M copper chloride in 9 M LiCl solution, collecting efficiency = 100%.

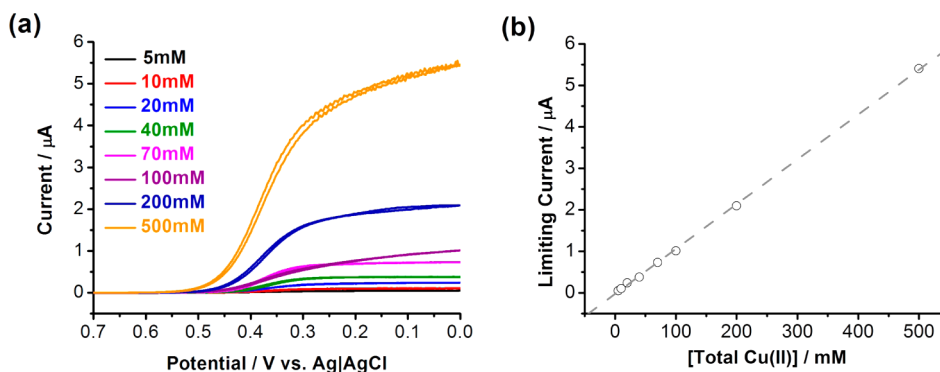


Figure 6. (a) Voltammograms of various concentration of copper chloride in 2.5 M NaCl with 1% HCl on a 25 μm platinum microelectrode at 80 $^{\circ}\text{C}$, at 50 mV/s and (b) calibration curve for part a.

concentrations of Cu(II) was attributed to formation of insoluble CuCl, experiments were carried out with much higher chloride concentrations, 9 M LiCl (without added HCl), since such conditions should favor formation of soluble complexes, e.g., CuCl_2^- . Under these conditions, both macroelectrodes and UMEs showed good voltammetry even at 1.5 M Cu(II). Multiple scans showed no change of the voltammetry after 1 h (Figure 4a,b). With the UME, the limiting current varied with near linear behavior with concentration (Figure 4d). The peak current on the macroelectrode varied with the square root of scan rate, $v^{1/2}$, indicating the redox reaction is diffusion controlled (Figure 4c). As discussed in the next section, the deviation of the limiting current with the UME from linearity in Figure 4d is caused by migrational effects.

The differences between the 2.6 and 9 M chloride for the Cu(II) reduction were thus quite dramatic. In the 2.6 M chloride solution, the analysis of copper was limited to the tens of millimolar range; whereas in the 9 M chloride solution, this was extended to the molar range.

The effect of chloride concentration and CuCl precipitation could also be observed in scanning electrochemical microscopy (SECM) experiments (Figure 5). Here a Pt tip electrode (radius, a , 12.5 μm) and a Pt substrate ($a = 50 \mu\text{m}$) were held at a distance, d or 10 μm , where the collection efficiency, N_{ss} ($-i_{\text{s}}/i_{\text{T}} \times 100$) for FcMeOH (ferrocene methanol) oxidation and FcMeOH⁺ reduction at the substrate was 100%.²⁸ With the substrate electrode held at a potential of 0.6 V, Cu(I) generated at the tip was oxidized at a diffusion-controlled rate to Cu(II) at the substrate. In the 2.6 M chloride system, even with a 10 mM cupric chloride concentration, the tip voltammogram was

distorted and showed an N_{ss} of Cu(I) at the substrate of 97%; the gradual loss of 3% can be attributed to surface precipitation of CuCl, which does not reach the substrate electrode (Figure 5a). In comparison, a 0.7 M cupric chloride in 9 M LiCl solution showed a better defined tip voltammogram and 100% collection efficiency (Figure 5b). The additional question of migration effects in SECM will be discussed elsewhere.

High Concentration Cupric Chloride in 2.5 M NaCl and 0.1 M HCl Solution at 80 $^{\circ}$. Since the solubility of CuCl should increase with temperature,²⁹ the surface precipitation effect was also studied at 80 $^{\circ}\text{C}$. The voltammetry of 0.5 M cupric chloride at 80 $^{\circ}$ (Figure 6a) can be compared to the same system at room temperature (Figure 2d). Clearly the higher temperature voltammogram is better defined and produces a limiting current vs concentration curve that is more suitable for voltammetric analysis of high concentrations of Cu(II). However even at high temperature, some precipitation of CuCl on the UME surface still exists, but the rate of precipitation was much slower than at room temperature.

Migration Effects on Reduction of Positively Charged Cu(II) Species. In most voltammetric analyses, the ratio of supporting electrolyte to electroactive species concentrations is large (>50–100) so that migrational effects on the electrochemical response are very small and mass transfer only by diffusion can be assumed. However in dealing with high concentrations of copper chloride solutions, migration effects can be significant, because the concentration of supporting electrolyte cannot attain required levels due to solubility limitations. Thus in considering the limiting current vs concentration curves under these conditions, e.g., Figure 4d, migration effects must be taken into account. The migration

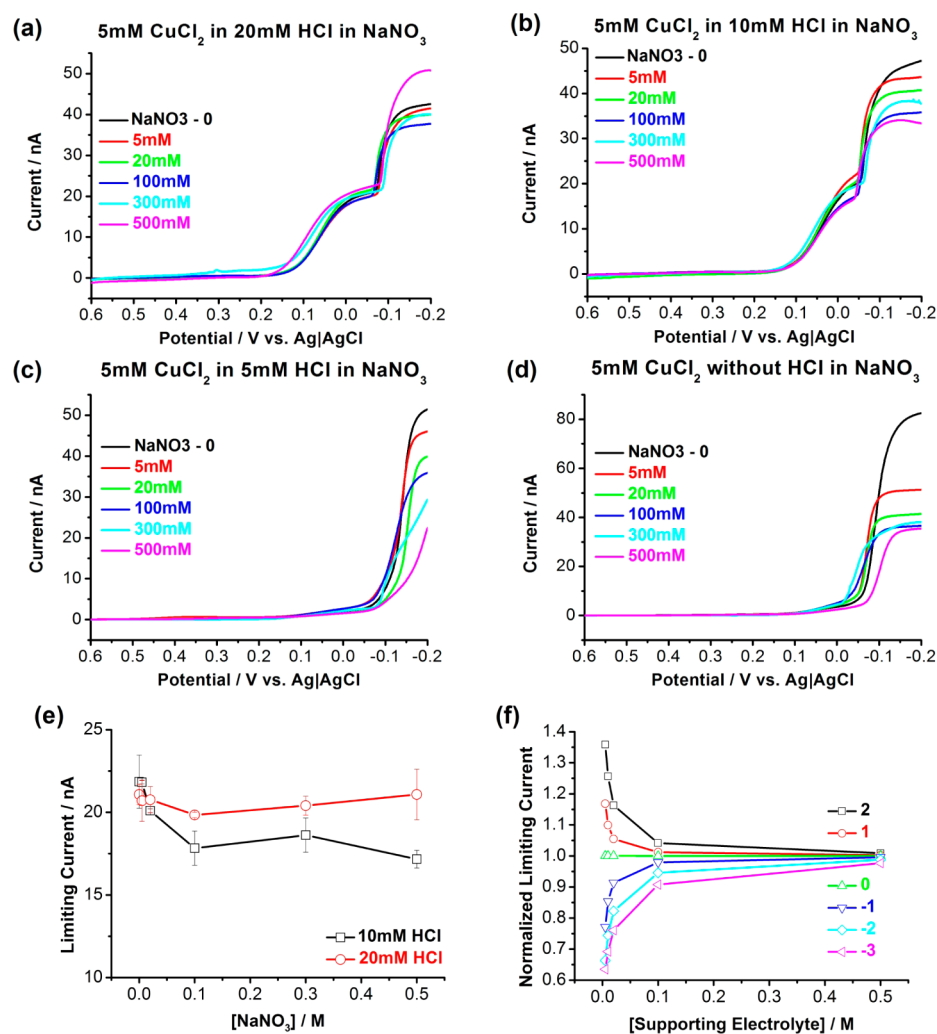


Figure 7. (a) Cyclic voltammograms (CVs) of 5 mM CuCl₂: (a) 20 mM HCl; (b) 10 mM HCl; (c) 5 mM HCl; (d) 0 mM of HCl all with various concentrations of NaNO₃ using a 25 μ m platinum UME at a scan rate of 10 mV/s; (e) the mean and standard deviation of limiting current of Cu(II) to Cu(I) reduction with different concentrations of HCl and NaNO₃, consistent with an average number of Cl ligands of 1 to 2 from Figure 1a; (f) results of a simulation of 5 mM analyte with different charges with a different concentration of supporting electrolyte considering diffusion and migration.

effect is driven by the reduction reaction that forms the production of negative charge in the solution near the electrode. This charge is compensated by the movement of ions: positive ions toward the electrode and negative ions away from it. Note also that the direction of the effect can also be useful in understanding speciation, i.e., CuCl₄²⁻ and CuCl₃⁻ will show smaller limiting currents on reduction than those predicted by diffusion, while CuCl₂ will be unaffected and CuCl⁺ will produce larger currents. That is why the migration model predicts slightly lower current at high concentration (Figure 4d).

At very high analyte concentration, the change of the solution viscosity can also affect the diffusion coefficient and limiting current (Figure 4d). The viscosities of deionized water, 9 M LiCl, 0.07 M CuCl₂ in 9 M LiCl, 0.7 M CuCl₂ in 9 M LiCl, and 1.5 M CuCl₂ in 9 M LiCl were measured using a standard viscometer at 25 °C. The results showed a viscosity change from 3.75 mPa·s for 0.07 M CuCl₂ in 9 M LiCl to 3.80 mPa·s for 0.7 M CuCl₂ in 9 M LiCl, and to 4.00 mPa·s for 1.5 M CuCl₂ in 9 M LiCl. This means that the diffusion coefficient of the high concentration Cu(II) solution (1.5 M CuCl₂ in 9 M LiCl) is about 9% smaller than the ones in diluted Cu(II)

solution (0.07 M CuCl₂ in 9 M LiCl). Thus the viscosity does affect the linearity in Figure 4d, but the change in limiting current cannot be accounted for by viscosity changes alone. At high concentration (1.5 M CuCl₂), the limiting current is about 25% less than prediction, without considering migration or viscosity change. Overall, the change of linearity in Figure 4d was caused by the combined effect of migration and viscosity.

To demonstrate the migration effect on reduction of positively charged Cu(II) species, we studied the effect of supporting electrolyte concentration on the voltammetry similar to earlier experiments, e.g., by White et al.¹⁵ In their work, the migration effect on the oxidation of TTF and the reduction of TCNQ was studied. In this work, since the original molecules are neutral, the limiting current from the first electron transfer reaction steps were unaffected by the supporting electrolyte concentration. However, the limiting current of the second waves decreased when the concentration of the supporting electrolyte decreased because of the repelling migration force. A number of other authors also studied migration effects in experimental and computational studies.^{15–18,30–34} In our work, the CV of 5 mM Cu(II) with different concentrations of HCl (0, 5, 10, and 20 mM) with

various concentrations of NaNO₃ (0–0.5 M) were studied. The concentration of HCl controlled the speciation while the NaNO₃ affected the migration. Forward voltammetric scans are shown in Figure 7. With 20 mM added HCl, the first reduction waves show Cu(II) to Cu(I) reduction, and the second reduction waves are due to Cu(I) to Cu(0). The second wave shows a Cu metal stripping wave on scan reversal (not shown).

With added 0 and 5 mM HCl and 5 mM CuCl₂, although the total Cl⁻ are 10 and 15 mM, the free Cl⁻ concentration is only a few millimolar, which is insufficient to produce the $n = 3$ and 4 chlorocomplexes (Figure 1a) and hence only the direct two-electron reduction to Cu(0) is seen (Figure 7c,d). Even with 10 mM added HCl solution, the Cu(II) to Cu(I) reduction current is smaller than that in the 20 mM HCl solution, signaling only partial conversion to the higher complexes. The species of Cu(II) chloride complexes in the 10 mM HCl and 20 mM HCl should be a mixture of Cu²⁺, CuCl⁺, CuCl₂, and CuCl₃⁻, according to Figure 1a. The limiting current of Cu(II) to Cu(I) reduction in 20 mM HCl did not change significantly with a different concentration of supporting electrolyte (Figure 7e), suggesting that the average charge of the original species is near zero, i.e., the migrational effects of the positively charged species canceled those of the negatively charged species. However, in the 10 mM HCl solution, the limiting current increased when reducing the supporting electrolyte concentration, which means the average charge of the species was slightly positive. The error bars in Figure 7e may be caused by experimental errors that include the small changes of analyte concentration or UME surface. In the 5 mM and 0 M HCl solutions, the reduction current of Cu(II) to Cu(0) decreased when increasing the supporting electrolyte concentration, which suggested the original Cu(II) species in those conditions were positively charged, mostly Cu²⁺ according to Figure 1a.

Numerical simulations of the migration effect were carried out to compare with the experimental data, part f vs part e of Figure 7.²² The advantage of this model is that, given the concentration of analyte and supporting electrolyte, by fitting the simulation curve, the average charge of the analyte can be found. This numerical model considers the diffusion and migration of charged species on a microelectrode. Briefly, the simulations were done using the Nernst–Planck with Electro-neutrality (NPE) application mode of the Chemical Engineering Module in Multiphysics v3.5a. The two solved equations were the Nernst–Planck equation (eq 1) and the electro-neutrality condition (eq 2):

$$J_i(r, z) = -D_i \nabla C_i(r, z) - \frac{z_i F}{RT} D_i C_i(r, z) \nabla \phi(r, z) \quad (1)$$

where J is the flux of the species i , D is the diffusion coefficient, C is the concentration, z is the charge on the species i in signed units of electronic charge, F is the Faraday constant, ϕ is the electric potential responsible for the migration effect, and other symbols have their usual meaning.

$$\sum_i z_i C_i = 0 \quad (2)$$

where z is the charge and C is the concentration of the species i . All other relevant equations, which include the initial and boundary conditions, are described elsewhere.²²

Overall the results show that migration is an important component of mass transfer at high (\sim molar) concentrations of Cu(II), even with 9 M supporting electrolyte concentrations. Moreover, the observation and simulation of migration effects

can provide information about the charge on the electroactive species.

CONCLUSIONS

The predominant species of Cu(II) complexes in high free chloride concentrations (>1 M) is CuCl₄²⁻, while for Cu(I) they are CuCl₂⁻ and CuCl₃²⁻. Voltammetry with an UME produces a good calibration curve even at high Cu(II) concentrations that can be used to measure the copper concentration with good precision. Interference from CuCl precipitation on the electrode that affects the voltammetric behavior at 2.6 M free chloride concentrations at room temperature can be mitigated by performing the experiment at 80 °C or by increasing the free chloride concentration to 9 M LiCl. At high Cu(II) concentrations, migration effects are observed, even in 9 M supporting electrolyte. By studying the limiting current as a function of supporting electrolyte concentration, the charge of the electroactive species can be determined by fitting experimental data to simulations of a migration model.

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Notes

The authors declare no competing financial interest.

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