# Measurement of Temperature-Dependent Stability Constants of Cu(I) and Cu(II) Chloride Complexes by Voltammetry at a Pt Ultramicroelectrode

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ABSTRACT: Cu(II)Cl complexes can undergo stepwise electrochemical reduction to Cu(I)Cl and then to Cu. In this paper, the Nernst equation is used to simultaneously calculate the temperature-dependent stability constants of both mononuclear Cu(II)Cl and Cu(I)Cl complexes for the first time. First, voltammograms were recorded at a Pt ultramicroelectrode (UME) with a variable of free chloride concentration at a given temperature. Using the equilibrium of Ag/AgCl redox couple, the free chloride activities were measured on an Ag electrode in different NaCl solutions, adjusting for the influence of ionic strength. This electrochemical technique was proved to be feasible at 25 and 90 °C. With increasing temperature, the Cu(II)Cl complex favored a lower coordination number and the $CuCl_2$ complex prevailed, whereas the $CuCl_4^{2-}$ was predicted to be unstable. The $CuCl_2^-$ and $CuCl_3^{2-}$ complexes were still the primary species for the Cu(I)Cl complex.
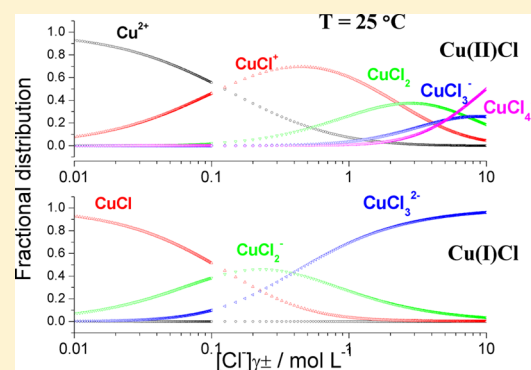
In aqueous solution, both Cu^{2+} and Cu^+ coordinate with Cl^- to form a series of Cu(II)Cl and Cu(I)Cl complexes.[1−3] We are interested in investigating the kinetics of the electrochemical reactions involving these complexes and especially the role of ligand-coupled electron transfer, e.g., when reduction of a Cu(II)Cl complex involves loss of a chloride ion. To carry out such investigations, it is necessary to have accurate distribution diagrams of these species. The properties of these complexes are also of special interest in coordination chemistry.[4,5] Sukhova et al.[6] first attempted to infer all the possible mononuclear and polynuclear Cu(I)Cl complex species as well as the corresponding stability constants, but every value seriously disagreed with the later recognized range.[2,7,8] It is reported that in chloride solutions below ∼5 M NaCl at ambient temperature, the major species of Cu(I)Cl complex are CuCl, $CuCl_2^-$, and $CuCl_3^{2-}$. Comparatively, four types of the weak mononuclear Cu(II)Cl complexes are presented, including $CuCl^+$, $CuCl_2$, $CuCl_3^-$, $CuCl_4^{2-}$. The polynuclear complex species can be ignored under this condition even with Cu(I) concentrations up to 1 M.[3,8−10]

Many determinations of stability (formation) constants for Cu(II)Cl and Cu(I)Cl complexes have been carried out based on solubility,[2,8,11] cation exchange,[12] or spectrophotometry,[7,13,14] but the reported values vary considerably. This problem arises from several aspects, such as excessive simplification, technical difficulties, or improper experimental designs. Some authors only provided one concentration to be studied for the determination of stability constant and underestimated the influence of ionic strength. However, many concentration variations, as well as the influence of

ionic strength, are required to calculate such competitive thermodynamic equilibria of complex formation.[3,14,15] Technical issues can also arise. For example, the spectrophotometric absorption bands for Cu(I)Cl complex species were reported to strongly overlap in the range of 250−280 nm, and the spectral deconvolution technique was insufficient for high precision.[9,16] Another technical issue is the low sensitivity to detect a small amount of complex fraction. The testing uncertainty of $CuCl_4^{2-}$ species has been already illustrated in prior works.[3,14] Besides, some unexpected side reactions may occur under improper experimental conditions, such as Cu^{2+} hydrolysis[17] or Cu^+ disproportionation.[18,19]

High-temperature conditions result in worse agreement for the measurement of stability constants. Cu(I)Cl complex species like CuCl were considered to be of singular importance by Crerar and Barnes in aqueous solution at temperatures between 200 and 350 °C.[20] Another report showed that $CuCl_2^-$ and $CuCl_3^{2-}$ were predicted as the principal species in the Cl^--rich solution up to 300 °C.[21] Besides, Sherman reported that $CuCl_3^{2-}$ was unstable toward dissociation into $CuCl_2^-$ and Cl^- at T > 125 °C, and he claimed that only the $CuCl_2^-$ species is significant.[22]

Although the application of voltammetry to determination of stability constants is classical, dating back to polarographic methods, relatively few studies have been described for systems with multiple simultaneous equilibria, such as those described

here. Moreover the novel use of a UME in such studies offers a number of advantages, such as the fact that steady-state currents are observed and potential errors caused by uncompensated resistance are minimized, allowing simple observation of the Nernstian behavior required for thermodynamic measurements. In the present work, a persuasive and systematic electro-chemical method is proposed to simultaneously determine stability constants of both mononuclear Cu(II)Cl and Cu(I)Cl complexes. The influence of ionic strength is successfully dealt with by the measurement of free chloride activity. The separated reference-electrode design is the key to apply this method at 90 °C.

■ EXPERIMENTAL SECTION

Chemicals. All chemicals from Fisher Scientific were reagent grade and used without further purification. All solutions were prepared with deionized Milli-Q water. The Ag/AgCl reference electrode (in 1 M KCl) was purchased from CH instruments Inc. Austin, TX.

Instruments and Measurement. The electrochemical experiments were carried out on either a model CHI660 workstation (CH instrument, Inc., Austin, TX) or an Autolab PGSTAT 128N potentiostat/galvanostat (Metrohm Autolab B.V.). In addition, the high-temperature study was performed in a water-bath HCTB-3030 (OMEGA). A three-electrode cell was used involving a Pt UME as the working electrode (radius = 12.5 μm), a Pt wire as the counter electrode, and a homemade hydrogen reference electrode.

Dynamic Hydrogen Reference Electrode (DHRE). Briefly, the DHRE consisted of a glass tube connected to a cylindrical porous vycor plug. A heat shrink tube was used to make a good seal at this connection. The H_2SO_4 (0.5 M) was injected into the glass tube, and a clean Pt wire was inserted. The assembly was carried out in a H_2-filled glovebag to remove trapped air. Finally, a rubber stopper was plugged into the unsealed side of the glass tube, where vacuum glue was used for air tightness. The hydrogen concentration inside the tube can be fine-tuned by electrochemical proton reduction on the Pt wire. The waves for 1 mM ferrocene (with supporting electrolyte, 0.1 M tetrabutylammonium perchlorate, in acetonitrile) have been recorded at a Pt UME to standardize the different batches of DHREs, compared with a standard commercial Ag/AgCl reference electrode at 25 °C.[23] If the half wave potential of ferrocene oxidation was shifted by more than 5 mV, the corresponding DHRE need to be refreshed. It was typically stable for 2−3 days.

■ THEORY

The successive reductive waves of the Cu(II)Cl reduction are described as

$$Cu^{2+} + e^- \rightleftarrows Cu^+ \tag{1.1}$$

$$Cu^+ + e^- \rightleftarrows Cu \tag{1.2}$$

The Nernst equations are given as

$$E = E_{s,21}^0 + \frac{2.3RT}{F} \log \frac{[Cu^{2+}]\gamma_{Cu^{2+}}}{[Cu^+]\gamma_{Cu^+}} \tag{2.1}$$

$$E = E_{s,10}^0 + \frac{2.3RT}{F} \log \frac{[Cu^+]\gamma_{Cu^+}}{\alpha_{Cu}} \tag{2.2}$$

where $E_{s,21}^0$ and $E_{s,10}^0$ are the standard electrode potentials of the Cu^{2+}/Cu^+ and Cu^+/Cu couples, respectively; $[Cu^{2+}]$ and $[Cu^+]$ represent the free concentrations of copper ions; $\gamma_{Cu^{2+}}, \gamma_{Cu^+}$ are individual ion activity coefficients for Cu^{2+} and Cu^+; α_{Cu} is the activity of copper. At 25 °C, the activity coefficient, γ, is expressed as

$$\log \gamma = -\frac{A|z_n|I^{1/2}}{1 + B\xi I^{1/2}} + f(B)I \tag{3.1}$$

where $f(B)$ is the deviation function of Helgeson,[24] z_n is ion charge, ξ is the Debye−Hückel distance of closest approach parameter, and I is ionic strength. Ionic strength, proposed as the major factor in this system, is determined by the stoichiometric concentration of cations and anions in the solution. Since the total concentration of copper ion was deliberately maintained at 5 mM, compared with the applied NaCl concentration, it gave a minimal contribution to ionic strength. $\gamma_{Cu^{2+}}$ and γ_{Cu^+} were simplistically replaced by the average ion activity coefficients, $\gamma_\pm$.

The total (analytical) copper concentration is the sum of all the copper species presented in the solution.

$$C_{Cu}^{II} = [Cu^{2+}] + \sum_n^{j=1} \beta_{II,j}[Cu^{2+}][L]^j \gamma_\pm^j \tag{4.1}$$

$$C_{Cu}^{I} = [Cu^+] + \sum_n^{j=1} \beta_{I,j}[Cu^+][L]^j \gamma_\pm^j \tag{4.2}$$

Here, stability constants of $Cu^{II}L_j$ and Cu^IL_j complexes, $\beta_{I,j}, \beta_{II,j}$, are defined as

$$\beta_{II,j} = \frac{[Cu^{II}L_j]}{[Cu^{2+}][L]^j} \frac{\gamma_\pm}{\gamma_\pm \gamma_\pm^j} \tag{5.1}$$

$$\beta_{I,j} = \frac{[Cu^IL_j]}{[Cu^+][L]^j} \frac{\gamma_\pm}{\gamma_\pm \gamma_\pm^j} \tag{5.2}$$

Combining eqs 2 and 4, we obtain

$$E = E_{s,10}^0 - \frac{2.3RT}{F} \log[1 + \sum_n^{j=1} \beta_{I,j}[L]^j \gamma_\pm^j]$$
$$+ \frac{2.3RT}{F} \log \frac{C_{Cu}^I \gamma_\pm}{\alpha_{Cu}} \tag{6.1}$$

$$E = E_{s,21}^0 + \frac{2.3RT}{F} \left\{ \frac{\log[1 + \sum_{j=1}^n \beta_{I,j}[L]^j \gamma_\pm^j]}{\log[1 + \sum_{j=1}^m \beta_{II,j}[L]^j \gamma_\pm^j]} \right\}$$
$$+ \frac{2.3RT}{F} \log \frac{C_{Cu}^{II} \gamma_\pm}{C_{Cu}^I \gamma_\pm} \tag{6.2}$$

Experimentally, voltammetry can be used to record the half wave potentials of both reduction waves for Cu(II) to Cu(I) and Cu(I) to Cu(0) as a function of $[Cl^-]\gamma_\pm$. These are then plotted as a function of $\log[L]$. To simplify the data treatment, one can take any region of free Cl^- concentration and one form of complex as predominant under these conditions. The regions including more than two forms of complex are assumed to be narrow enough. Equation 6.1 is then simplified to

Table 1. Mean Average Activity Coefficients $(\gamma_\pm)^{25}$ As a Function of NaCl Concentration at 25 and 90 °C

C_{NaCl} (mol/L)	0.001	0.005	0.01	0.25	0.05	0.1	0.4	0.8	1	1.5	2.5
$\gamma_\pm$ (25 °C)	0.965	0.926	0.899	0.85	0.808	0.778	0.693	0.693	0.662	0.657	0.668
$\gamma_\pm$ (90 °C)	0.965	0.925	0.899	0.848	0.798	0.75	0.66	0.634	0.63	0.634	0.667

$$E = \left(E^0_{s,10} + \frac{2.3RT}{F} \log C^I_{Cu}\gamma_\pm - \frac{2.3RT}{F} \log \beta_{I,j} \right) - \frac{2.3jRT}{F} \log([L]\gamma_\pm) \tag{7.1}$$

For any form of complex, a linear relationship between E and $\log([Cl^-]\gamma_\pm)$ with a corresponding slope of $2.3jRT/F$ can be found in a certain region. Then, an estimate of the $\beta_{I,j}$ values can be obtained from these intercepts. Next, all the obtained $\beta_{I,j}$ values are substituted into eq 6.2. Using four groups of $E_{1/2 \, [Cu(II) \, to \, Cu(I)]}$ and $\log([Cl^-]\gamma_\pm)$ values, four-variable linear equations are set up and then the $\beta_{II,j}$ values can be solved. In order to improve the accuracy, the selection of four groups must disperse enough to imply the change of the Cu(II)Cl complex formation as a function of $[Cl^-]\gamma_\pm$.

■ RESULTS AND DISCUSSION

Measurement of Free Chloride Activity, $[Cl^-]\gamma_\pm$. The free chloride ion concentration at a given temperature is determined by the solubility product of AgCl (K_{sp}) and the stability constants (β_j) of silver chlorocomplexes. Taking into account the influence of the activity coefficients, they should be defined as

$$K_{sp} = [Ag^+][Cl^-]\gamma_\pm^2 \tag{8.1}$$

$$\beta_2 = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} \frac{1}{\gamma_\pm^2} \tag{8.2}$$

$$\beta_3 = \frac{[AgCl_3^{2-}]}{[Ag^+][Cl^-]^3} \frac{1}{\gamma_\pm^3} \tag{8.3}$$

Because of the low solubility of AgCl, $[Ag^+]$ has little contribution to the ionic strength. The average activity coefficient, $\gamma_\pm$, in eq 8 is considered to depend on the concentration of NaCl. In terms of charge balance,

$$[Ag^+] + [Na^+] = [Cl^-] + [AgCl_2^-] + 2[AgCl_3^{2-}] \tag{9.1}$$

Substituting eqs 8.2 and 8.3 into 9.1, we obtain

$$[Ag^+] + [Na^+] = [Cl^-] + \beta_2[Ag^+][Cl^-]^2\gamma_\pm^2 + 2\beta_3[Ag^+][Cl^-]^3\gamma_\pm^3 \tag{10.1}$$

Table 1 lists the mean average activity coefficients ($\gamma_\pm$) as a function of NaCl concentration. Table 2 shows the literature values of solubility of AgCl, the standard electrode potential of Ag/Ag$^+$, and the stability constant of chlorosilver complex

Table 2. Solubility of AgCl, Stability Constant of Chlorosilver Complex Species and Standard Electrode Potential of Ag/Ag$^+$, as Reported in the Literature[26,27]

|	K_{sp} (AgCl)	$\log \beta_2$	$\log \beta_3$	E_f^0/V
25 °C	1.85×10^{-10}	5.18	5.45	0.7993
90 °C	2.23×10^{-8}	4.46	3.85	0.71

species.[26] By means of eq 8.1 and 10.1, the values of $[Ag^+]$ and $[Cl^-]$ are unique for any NaCl concentration.

The equilibrium of Ag/Ag$^+$ couple is described by the Nernst equation

$$E_{eq} = E^0_{(Ag/Ag^+)} + \frac{RT}{F} \ln(\gamma_\pm[Ag^+]) \tag{11.1}$$

where $E^0_{(Ag/Ag+)}$ is the standard electrode potential of Ag/Ag$^+$ couple at a given temperature and E_{eq} is the equilibrium potential. It is seen that the values of E_{eq} and $[Cl^-]\gamma_\pm$ correspond to each other uniquely.

Figure 1 gives both theoretical prediction (black triangles) and experimental data (red squares) of the relationship
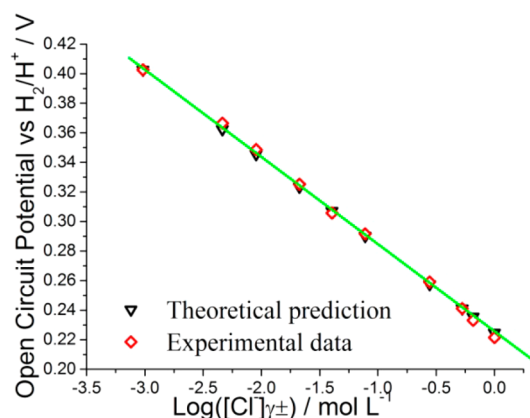
Figure 1. Experimental relationship of E_{eq} and $\log([Cl^-]\gamma_\pm)$, tested on an Ag electrode vs DHRE in different NaCl solutions at 25 °C, in agreement with the theoretical prediction.

between E_{eq} and $[Cl^-]\gamma_\pm$. The theoretical calculation uses the weight of NaCl to calculate the equilibrium potential of Ag/Ag$^+$ couple. The experimental data were measured on an Ag electrode vs DHRE in NaCl solution at 25 °C, where each open circuit potential (OCP) measurement took 60 s with a precision of better than ±1 mV. Longitudinally translating the experimental data by +8 mV (caused by the influence of the DHRE), it conforms well to the theoretical prediction.

No matter what kind of the metal ion is involved, its contribution to ionic strength in this work is negligible, so the $\gamma_\pm$ value is merely decided by the specific NaCl concentration. In other words, the determination of $[Cl^-]\gamma_\pm$ is transformed into the OCP measurement on an Ag electrode in a given solution. This measurement is more easily achieved and still contains the details of ionic strength.

Measurement of Stability Constant at 25 °C. Copper-chloride-complex samples were prepared with 5 mM CuSO$_4$, 10 mM HCl, and various concentrations of NaCl ranging from 0.001 to 5 M. The HCl was used to prevent formation of hydroxy complex, and it helped dissolve the CuCl. Before recording the voltammogram of Cu(II) reduction, an OCP measurement was performed to give the $[Cl^-]\gamma_\pm$ value of each testing solution and the Pt UME needed to be carefully polished to remove Cu-contamination.

A typical voltammogram of Cu(II)Cl reduction was recorded in Figure 2 (red) on a platinum electrode in the presence of 1
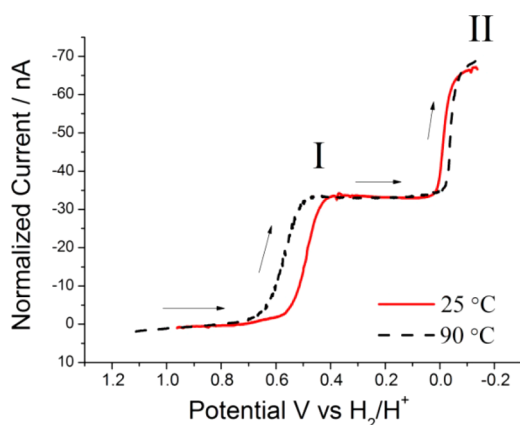

Figure 2. Typical voltammogram of 5 mM CuSO$_4$ reduction in aqueous solution containing 10 mM HCl and 1 M NaCl on a platinum electrode vs DHRE at 25 and 90 °C; ν = 100 mV s^{-1}.

M NaCl vs DHRE at 25 °C. The first wave at 0.5 V exhibited the Nernst behavior of the Cu^{2+}/Cu$^+$ couple. Subsequently, Cu deposition appeared and reached a steady state current on the forward sweep and Cu was stripped on the backward sweep.[4,28] As the concentration of NaCl increased, the first wave shifted to more positive potential, and the second one simultaneously shifted negatively.

Figure 3 displays a series of half wave potentials for both reduction processes (like Figure 2) as a function of the corresponding $[\text{Cl}^-]\gamma_\pm$. It is reasonable to give three slashes to represent the three dominant species (CuCl, CuCl$_2^-$, and CuCl$_3^{2-}$)^2 in turn. These slopes (63, 118, and 174 mV derived from Figure 3B) are in accordance with the factor 2.3nRT/F (n = 1, 2, 3). In eq 7.1, three factors make up the intercept, and two of them are known: the formal potential of the Cu$^+$/Cu couple is 0.52 V vs NHE 25 °C and the total amount of copper ions remains constant. According to a previous study of the activity coefficient of a NaCl solution,[29] the $\gamma_\pm$ value can be approximately inferred at a given temperature. Therefore, the $\beta_{\text{I},j}$ values can be calculated. All stability constants are summarized into Table 3.

As discussed previously, three $\beta_{\text{I},j}$ values were substituted into eq 6.2, and four groups of $E_{1/2}$ and log($[\text{Cl}^-]\gamma_\pm$) values were

Table 3. Summary of Stability Constants of Copper Chloride Complexes at 25 °C

j	1	2	3	4
log $\beta_{\text{I},j}$ (Cu$^+$-nCl$^-$)	4.87	5.97	6.7	NA^a
log $\beta_{\text{II},j}$ (Cu^{2+}-nCl$^-$)	0.876	0.653	−0.082	−1.416

^{a}CuCl$_4^{3-}$ is not present.

selected from Figure 3A. The stability constants of the Cu(II)Cl complexes, $\beta_{\text{II},j}$, were calculated from four-variable linear equations and the results are listed in Table 3. Compared with the literature values at 25 °C, our values for the Cu(II)Cl and Cu(I)Cl complexes fall into a reasonable range.[2,3,8]

As Ramette previously reported, the CuCl$_4^{2-}$ complex comprised of a small fraction of the total copper even when the chloride concentration reached 5 M and no precise estimate of the $\beta_{\text{II},4}$ value could thus be obtained.[15] Schwing-Weill attempted to determine four stability constants of Cu(II)Cl complexes, using the spectrophotometric technique, but the $\beta_{\text{II},4}$ value was also not successful to be determined.[30] In contrast, the electrochemical response is more sensitive to capture a tiny signal change, and it allows the $\beta_{\text{II},4}$ value to estimate more precisely.

Measurement of Stability Constant at 90 °C. In order to measure the stability constant at 90 °C, the sealed electrochemical cell was completely immersed into a thermostatic bath at all times. The water bath needed to be turned off during the measurement to minimize the noise, but such operation caused a temperature fluctuation of ±2 °C. The real problem in extending this experiment to 90 °C was the stability of the reference potential. An alternative design was used where the reference electrode was held at room temperature and removed from the test cell, and a salt bridge was used to connect the two (a capillary filled with saturated NaCl). This design helped stabilize the reference potential at 90 °C.

Figure 4 shows the theoretical (black) and experimental (red) relationship between E_{eq} of the Ag/Ag$^+$ couple and log($[\text{Cl}^-]\gamma_\pm$) at 90 °C. Each test of the OCP lasted for 60 s with precision better than ±2 mV. The experimental data required a longitudinal translation of −0.005 V to get the best fit with the theoretical prediction.

By means of this relationship, the $[\text{Cl}^-]\gamma_\pm$ value in every solution of Cu(II)Cl complexes at 90 °C can be measured. Duplicating the processes carried out at 25 °C, the stepwise reduction of Cu(II)Cl complex at 90 °C was recorded, using
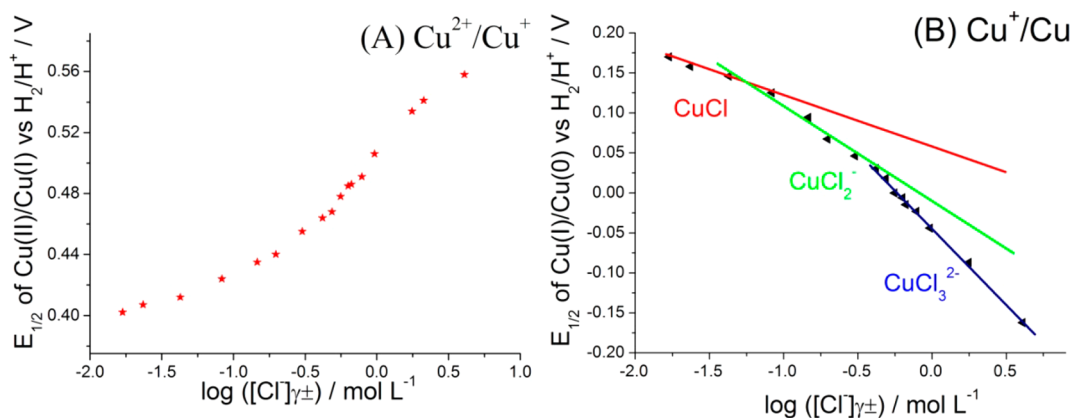

Figure 3. Plot of half wave potentials of Cu(II) reduction to Cu(I) (A), then to Cu(0) (B) vs log($[\text{Cl}^-]\gamma_\pm$), tested in acidic aqueous solution on a Pt electrode at 25 °C; ν = 100 mV s^{-1}.
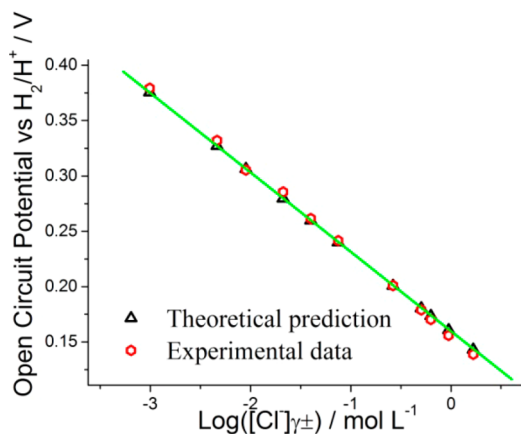
Figure 4. Experimental relationship of E_{eq} and $\log([Cl^-]\gamma_\pm)$ on an Ag electrode in NaCl solution at 90 °C vs DHRE at 25 °C, in agreement with the theoretical prediction.

voltammetry. A typical voltammogram is shown in Figure 2 (black), involving 1 M NaCl as the supporting electrolyte. Note that the current is normalized to offset a change in diffusion coefficient of electroactive species at different temperatures. Extending to 90 °C, the first wave shifted positively, yet the second one shifted negatively.

Figure 5 summarizes the half wave potentials of both Cu(II)Cl and Cu(I)Cl reduction as a function of $\log([Cl^-]\gamma_\pm)$ at 90 °C. The same analysis was carried out to obtain three slashes, where these slopes (approximately 74, 140, and 206 mV) are consistent with $2.3nRT/F$ ($n = 1, 2, 3$; $T = 363$ K). Similar to the case at 25 °C, the intercept in eq 7.1 is given by the electrode potential, the Cu(I)Cl activity, and the $\beta_{I,j}$ value. It is noted that the electrode potential, E^0, is approximately linear with temperature over a range of 0 and 100 °C.[31,32] With their temperature coefficients, E^0 of Cu$^+$/Cu and Cu^{2+}/Cu$^+$ couples are decided to be 0.45 and 0.231 V vs NHE at 90 °C, respectively. So the $\beta_{I,j}$ values can be calculated. The same mathematical treatment for eq 6.2 was used to determine the stability constants of Cu(II)Cl complex at 90 °C.

All the β values are shown in Table 4. The negative heats of the Cu(II)Cl and Cu(I)Cl complexes formation ranging from 15 to 100 °C reported by Fritz[33] and Muhammed[8] implied that the increasing temperature favors the dissociation of the complex, in agreement with the lower values of stability constant obtained at 90 °C.
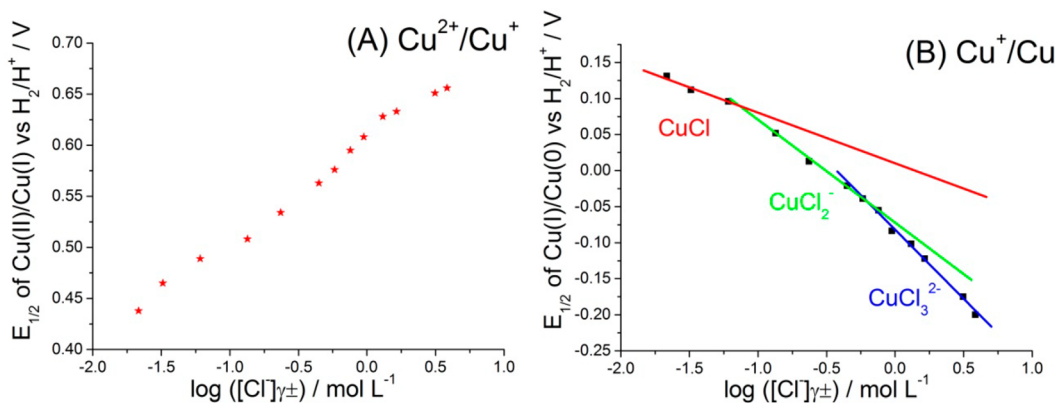
Table 4. Summary of Stability Constants of Copper Chloride Complexes at 90 °C

j	1	2	3	4
$\log \beta_{I,j}$ (Cu$^+$-nCl$^-$)	3.63	4.78	4.85	NA
$\log \beta_{II,j}$ (Cu^{2+}-nCl$^-$)	0.294	0.326	−1.082	−2.845

Fractional Distribution of Copper Chloride Complex. In acidic aqueous solution, four weak mononuclear Cu(II)Cl complexes are formed in turn as the chloride concentration is increased. The fractional distribution of Cu(II)Cl complex species depends on the free chloride activity at a given temperature, and each fraction is written as

$$\% CuCl_j^{2-j} = \frac{[CuCl_j^{2-j}]}{[Cu^{2+}] + \sum_{j=1}^{4} [CuCl_j^{2-j}]}$$

$$= \frac{[\beta_{II,j}[Cl^-]^j \gamma_\pm^j]}{1 + \sum_{j=1}^{4} \{\beta_{II,j}[Cl^-]^j \gamma_\pm^j\}} \qquad (12.1)$$

The value of $[Cl^-]\gamma_\pm$ is set as a consecutive array with an interval of 0.001 M.

Figure 6 shows the fractional distribution of Cu(II)Cl complex species plotted with $\log([Cl^-]\gamma_\pm)$ at 25 and 90 °C. At
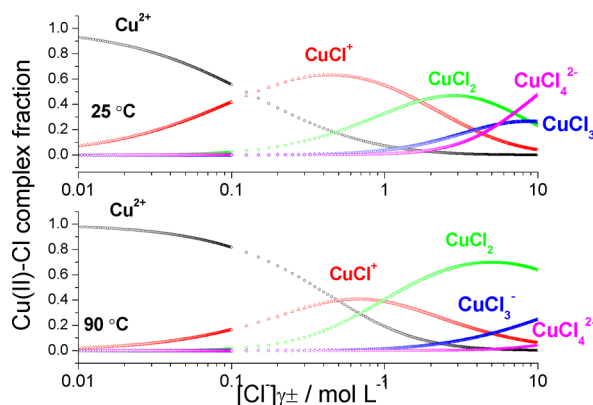

Figure 6. Fractional distribution of Cu(II)Cl complexes as a function of $\log([Cl^-]\gamma_\pm)$, the chloride activity, at 25 and 90 °C.

90 °C, the Cu(II)Cl complex favors to the lower coordination number and the CuCl$_2$ complex prevails. The increasing

Figure 5. Plot of half wave potential of Cu(II) reduction to Cu(I) (A), then to Cu(0) (B) vs $\log([Cl^-]\gamma_\pm)$, tested in acidic aqueous solution on a platinum electrode at 90 °C vs DHRE at 25 °C; $\nu = 100$ mV s^{-1}.

entropy of water and the decreasing activity coefficient of NaCl can cause it. The $CuCl_3^-$ complex at 25 °C is weakly stable because of a weak bond with the third Cl^-. The dissociation is greatly enhanced as the temperature is increased. In addition, almost no $CuCl_4^{2-}$ complex species can be observed at 90 °C in the NaCl solution. This conclusion is in contrast to the one reported by Liu and McPhail.[34] They predicted that the $CuCl_4^{2-}$ complex is dominant at 400 °C when the chloride concentration is more than 3 M.

The formation of the polynuclear Cu(I)Cl complex is negligible in this work, and each fraction of the mononuclear Cu(I)Cl complex is expressed by eq 13.1, where the $[Cl^-]\gamma_\pm$ value is assigned as the same consecutive array as above.

$$\%CuCl_j^{1-j} = \frac{[CuCl_j^{1-j}]}{[Cu^+] + \sum_{j=1}^{3}[CuCl_j^{1-j}]}$$

$$= \frac{[\beta_{1,j}[Cl^-]^j\gamma_\pm^j]}{1 + \sum_{j=1}^{3}\{\beta_{1,j}[Cl^-]^j\gamma_\pm^j\}} \qquad (13.1)$$

Figure 7 displays the fractional distribution of Cu(I)Cl complex species as a function of chloride activity at 25 and 90
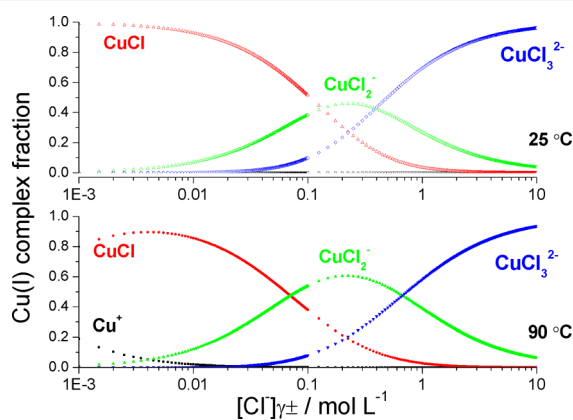

Figure 7. Fractional distribution of Cu(I)Cl complexes as a function of $\log([Cl^-]\gamma_\pm)$, the chloride activity, at 25 and 90 °C.

°C. Cu^+ is almost invisible at 25 °C but observed at 90 °C. The $CuCl_2^-$ and $CuCl_3^{2-}$ complexes are still the important species in the solution at 90 °C, but the fraction slightly favors the $CuCl_2^-$ species. According to Sherman's report, the $CuCl_3^{2-}$ complex gradually becomes unstable and dissociates into $CuCl_2^-$ and Cl^- when the temperature is increased. The $CuCl(H_2O)$ structure favors the increased Cl^- complexation to $CuCl_2^-$ due to the increasing entropy, predicted by molecular dynamics simulations.[22]

SUMMARY

The electrochemical reduction of the Cu(II)Cl complex on a Pt UME at 25 °C was voltammetrically recorded in the presence of difference NaCl concentrations. The half wave potentials of two consecutive reductive waves should conform to the Nernst equation as a function of free chloride activity, involving their stability constants. In terms of the equilibrium of the Ag/Ag^+ redox couple, free chloride activity was obtained from the approximately linear relationship with open circuit potential, tested an Ag electrode in specific Cu(II)Cl-NaCl solution, where the influence of ionic strength was accounted for. The

stability constants of both Cu(II)Cl and Cu(I)Cl complexes were simultaneously calculated by eqs 6.2 and 7.1.

This method can be extended to 90 °C with good consistency. Its success is caused by the alternative design of the three-electrode-system to maintain the reference potential. At 90 °C, the Cu(II)Cl complex favors the lower coordination number and the $CuCl_2$ complex prevails, whereas the $CuCl_4^{2-}$ complex is predicted to be unstable; $CuCl_2^-$ and $CuCl_3^{2-}$ are still the primary species for the Cu(I)Cl complex, but the fraction slightly favors to the $CuCl_2^-$ species.

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Notes

The authors declare no competing financial interest.

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