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ORIGINAL PAPER

# Influence of concentrations of copper, levelling agents and temperature on the diffusion coefficient of cupric ions in industrial electro-refining electrolytes

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**Abstract** Few data are available for diffusion coefficients measured in industrial copper electrolytes. In the present work the influence of copper concentration (19.9–58.1 g dm$^{-3}$), temperature (20–60°C) and concentrations levelling agents i.e. animal glue (0–5 mg dm$^{-3}$) and thiourea (0–5 mg dm$^{-3}$) on diffusion coefficients of copper was studied in industrial copper refinery electrolytes. Chronoamperometry at ultramicroelectrodes was used as an electrochemical technique. Apparent bulk diffusion coefficients were calculated on the basis of the theory of electrochemical nucleation on disc-shaped ultramicroelectrodes. Increasing copper concentration decreased the apparent bulk diffusion coefficient of copper and diffusion coefficients followed the Arrhenius temperature relationship. The experimental activation energy was 26.8 kJ mol$^{-1}$. The influence of levelling agents on diffusion coefficients was not strong in the studied concentration range of animal glue and thiourea.

**Keywords** Chronoamperometry · Diffusion coefficient of cupric ions · Industrial electro-refining electrolytes · Ultramicroelectrodes

## 1 Introduction

One of the most important and fundamental modes of mass transport during copper electro-refining is diffusion and data are available for cupric ion diffusion [1–9]. All the studies were carried out using laboratory prepared copper electro-refining electrolytes. It is believed that no systematic data are available in industrial electrolytes at different temperatures and copper ion concentrations. The composition of real industrial electrolyte is complex and is able to exert significant influence on copper diffusion coefficients. Commercial copper refining electrolytes contain usually 40–50 g dm$^{-3}$ copper, 170–200 g dm$^{-3}$ $H_2SO_4$, 0.02–0.05 g dm$^{-3}$Cl$^{-}$ and numerous impurities (e.g. 25 g dm$^{-3}$ Ni, 20 g dm$^{-3}$ As, 2 g dm$^{-3}$ Fe, 0.7 g dm$^{-3}$ Sb, 0.6 g dm$^{-3}$ Bi) and also 1–10 parts per million of levelling and grain-refining agents (e.g. animal glue and thiourea) [10]. The main aim of this investigation is to determine the diffusion coefficient of copper as a function of temperature, concentration of cupric ions and the levelling agents thiourea and animal glue in real electrolytes from copper refineries.

Chronoamperometry at ultramicroelectrodes (of 10$^{-6}$ m linear size) was used as an electrochemical technique. Mass transport rates to and from the ultramicroelectrode are increased because of non-planar diffusion. Non-linear diffusion to ultramicroelectrodes has many important practical implications [11–13]. As a result of its small size an ultramicroelectrode possesses a number of advantages such as high transport rate, low time constant relative to double layer charging and low value of ohmic resistance drop. Due to high currents, routinely used microelectrodes (of millimetre linear size) cannot be applied at such high current densities because of high ohmic resistance drop. High current densities result from the fact that chronoamperometric experiments were carried out at the potential where copper reduction is controlled by the diffusion, i.e. at the plateau of the voltammetric curve that is registered in industrial electrolyte at an ultramicroelectrode. Additionally, the observation time at microelectrodes would be long

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enough to introduce errors related to natural convection during mass transport. By using ultramicroelectrodes we can limit the experimental time to 84 ms.

## 2 Experimental

Experiments were conducted using a two-electrode configuration. A gold disc ultramicroelectrode of diameter 25 µm was employed as the working electrode. The auxiliary electrode was a copper plate of high purity (grade A, 99.99% Cu) with a surface of about 0.3 $\mathrm{cm}^2$. The auxiliary electrode also acted as the reference electrode. Chronoamperometric measurements were carried out using the AUTOLAB GSTST30 system (EcoChemie). General Purpose Electrochemical System version 4.5 was used for data acquisition. Potentiostatic current transients for electrodeposition of copper were registered at –0.4 V (vs. copper reference electrode) for 0.084 or 0.1 s.

The ultramicroelectrode was mechanically polished with wet alumina powder of grain diameter 0.3 and 0.05 µm. The surface of an ultramicroelectrode was observed using optical microscope. An smooth electrode was used for voltamperometric measurements in reference industrial electrolyte (without organic additives) in order to check the reproducibility of the voltammetric limiting current in the range of 1% standard deviation.

Industrial electrolytes from the KGHM S.A. copper refinery in Legnica (Poland) and Norddeutsche Affinerie, Hamburg, were used. Before measurements the electrolyte was heated (under reflux condenser) for 4 h in order to remove active animal glue and thiourea present in the industrial electrolytes. In order to study the influence of levelling agents, either fresh glue or thiourea were added in the concentration range 1–5 mg $\mathrm{dm}^{-3}$. The measurements were carried out 1 h after the addition of levelling agents. Consequently, steady state (equilibrium) hydrolysis processes, regarding levelling agents, were achieved and reproducible electrochemical results could be obtained.

## 3 Results

Typical current-time curves are shown in Fig. 1. In agreement with previously published data [14] the curves consist of three regions. The first corresponds to double-layer charging. The second is the induction region where no copper deposition is observed. In the third region copper nucleation takes place. This part of transient corresponds to the growth of the electroactive area as new nuclei are formed (or the nuclei surface area grows) and current rise is observed. The number of active sites for nucleation on the surface is limited therefore after the maximum; the current starts to decrease to the diffusion steady state value [16]. According to the nucleation models of metal at constant potential [14–16] the nucleation can be kinetic or diffusion-controlled. The description of current-time transients on ultramicroelectrodes requires different expressions from those used at conventional-sized electrodes [16]. Correira et al. [17] developed appropriate equations taking into account mass transport by spherical diffusion to disc-shaped ultramicroelectrodes. The current-time transient for progressive nucleation controlled by spherical diffusion is described by Eq. (1)

$$i = (nFD^{1/2}c^{\infty}r^2\pi^{1/2}t^{-1/2} + nFc^{\infty}rD\pi) \times [1 - \exp(-0.5\,AN_{\infty}\pi k'Dt^2)] \tag{1}$$

where $i$ is current, $n$ is the number of electrons transferred during the reaction, $F$ is Faraday's constant, $D$ is the diffusion coefficient, $AN_{\infty}$ is the rate of nuclei formation, $c^{\infty}$ is bulk concentration and $r$ is the radius of disc, $t$ is time, $k'$ is the numerical constant for progressive nucleation and is expressed by Eq.(2)

$$k' = 4/3(8\pi c^{\infty}M/\rho)^{1/2} \tag{2}$$

where $M$ is molar mass, $\rho$ is the copper density.

Eq. 1 was used in this work for the determination of diffusion coefficients by fitting simulated current-time transients to experimental curves. The part of curve which was taken into account was the third region were copper deposition is observed i.e. after the induction period presented in Fig. 1. In most cases the starting point for the fitting was around 1 ms after the measurement was initiated (constant potential applied). The fitting procedure was the trial and error method using two parameters: $D$ and $AN_{\infty}$. A sample result of the fitting is shown in Fig. 2. The kinetic parameters $AN_{\infty}$ obtained from the fitting are not discussed in this paper due to the limitation of volume and clarity. The detailed discussion of the copper reduction mechanism and kinetics will be presented in the subsequent paper where chronoamperometry results will be compared with those obtained by ac impedance at ultramicroelectrodes in the same electrolytes. The diagnostic criterion for accuracy was a very good agreement between experimental and fitted simulated curves, especially in the first part of the transient including the current maximum. The mean square errors (MSE) were calculated using the equation: $MSE(\theta) = \frac{1}{n}\sum_{j-1}(\theta_j - \theta)^2$ where $\theta_j$ is experimental current and $\theta$ is calculated current. Calculated MSE in reference to the diffusion current squared did not exceed 4%. Calculated and experimental curves were slightly different in the last part of curve. As reported [17] these differences might be caused by strong edge effect [18].

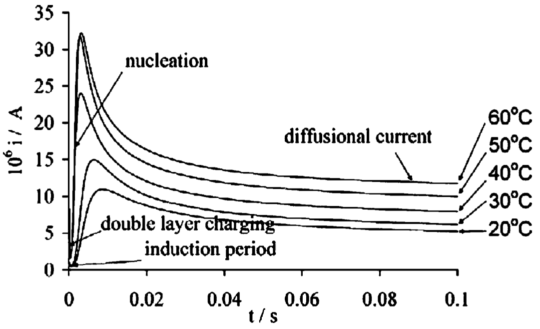

**Fig. 1** Chronoamperometric curves in industrial electrolyte at different temperatures. Electrolyte: 44.31 g $dm^{-3}$ Cu, added animal glue 1 mg $dm^{-3}$, without added thiourea

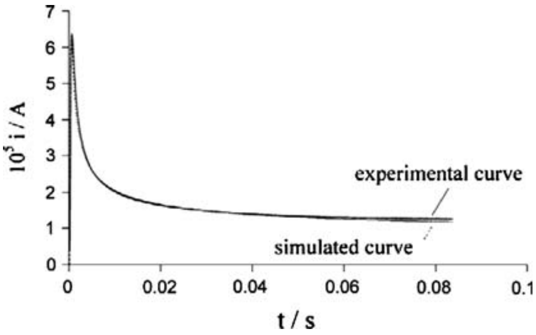

**Fig. 2** Experimental and simulated chronoamperometric curves. Industrial electrolyte: 41 g $dm^{-3}$Cu, without levelling agents, 60°C

### 3.1 Effect of copper concentration

The dependence of diffusion coefficient on copper concentration is listed in Table 1. As shown in Fig. 3 the parameter D decreases with increasing copper concentration from 19.9 g $dm^{-3}$ to 58.1 g $dm^{-3}$. At 40°C the relationship between D and cupric ion concentration is linear and is given by: $D_{Cu(II)} = -3 \times 10^{-8}[Cu^{2+}] + 8 \times 10^{-6}$

### 3.2 Effect of temperature

In industrial electrolytes containing 19.9–58.1 g $dm^{-3}$ copper, the influence of temperature in the range 20–40°C on the diffusion of cupric ions is shown in Fig. 4. The diffusion coefficients are strongly temperature dependent. In industrial electrolyte containing 44.3 g $dm^{-3}$ copper and in the range 20–40°C, parameter D follows the Arrhenius relationship expressed by Eq. (3).

$$D = D_o e^{(-E_D/RT)} \tag{3}$$

where $D_o$ is a pre-exponent, $E_D$ is the activation energy for the diffusion process, $R$ is the gas constant and $T$ is temperature in K. Using experimental data the following relation can be obtained: $\ln D = -3225.2\ (1/T) - 1.2544$ ($R^2 = 0.99$)

The activation energy of diffusion was estimated from the slope of the relation above and was found to be 26.8 kJ $mol^{-1}$ which is higher by about 7.6 kJ $mol^{-1}$ than estimated in synthetic electrolyte [3].

**Table 1** Effect of copper concentration and temperature on diffusion coefficient of cupric ion in industrial electrolyte

| [Cu]/g $dm^{-3}$ | $10^6$D/ $cm^2s^{-1}$ | | | |
|---|---|---|---|---|
| | 20°C | 25°C | 35°C | 40°C |
| 19.9 | 4.50 | 4.83 | 6.45 | 7.55 |
| 29.5 | 4.04 | 4.20 | 6.30 | 7.30 |
| 36.9 | 3.00 | 4.00 | 6.00 | 7.00 |
| 50.1 | 3.60 | 3.95 | 5.60 | 6.75 |
| 58.1 | 3.20 | 4.02 | 5.50 | 6.50 |

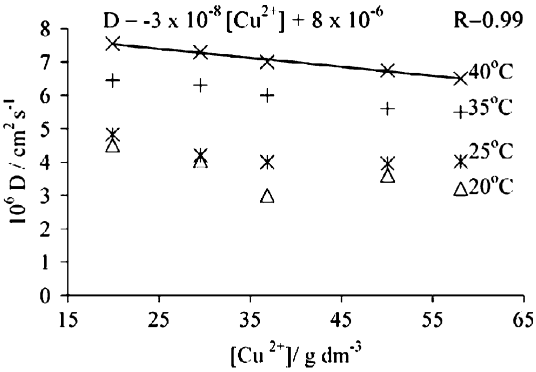

**Fig. 3** Diffusion coefficients as a function of cupric ion concentration. Industrial electrolyte: without added levelling agents

### 3.3 Effect of animal glue concentration

Diffusion coefficients calculated for electrolytes containing 0–5 mg $dm^{-3}$ animal glue are listed in Table 2. Animal glue did not affect the diffusion very strongly but a strong dependence on temperature was observed. Figure 5 illustrates the plot of D versus animal glue concentration.

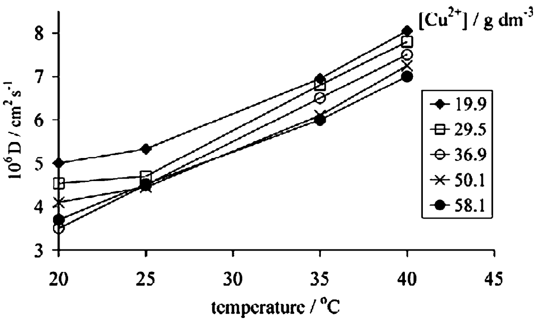

**Fig. 4** Diffusion coefficients as a function of temperature. Industrial electrolyte: without added levelling agents

**Table 2** Effect of glue concentration and temperature on diffusion coefficient of cupric ion in industrial electrolyte

| [animal glue]/ mg dm$^{-3}$ | $10^6$ D / cm$^2$ s$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 20°C | 30°C | 40°C | 50°C | 60°C |
| 0 | 4.75 | 6.87 | 9.37 | 14.0 | 17.3 |
| 1 | 4.86 | 6.60 | 9.00 | 13.6 | 14.2 |
| 2 | 4.73 | 6.56 | 9.10 | 12.4 | 18.4 |
| 3 | 5.66 | 7.15 | 9.99 | 14.2 | 17.6 |
| 4 | 5.50 | 7.15 | 10.3 | 14.1 | 18.7 |
| 5 | 5.43 | 7.05 | 10.7 | 14.2 | 19.3 |

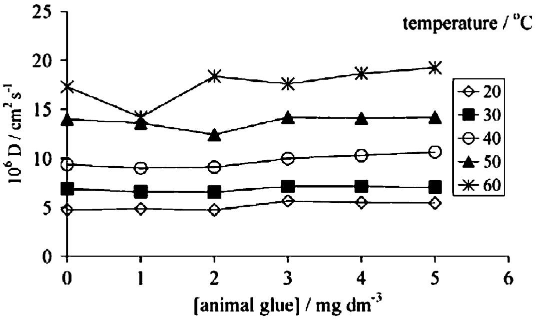

**Fig. 5** Diffusion coefficients as a function of added animal glue concentration. Industrial electrolyte: 43.3 g dm$^{-3}$ Cu, without added thiourea

### 3.4 Effect of thiourea concentration

Diffusion coefficients calculated for electrolytes containing 0–5 mg dm$^{-3}$ thiourea are listed in Table 3. The relation between D and thiourea concentration is illustrated at Fig. 6.

Thiourea (TU) undergoes a series of chemical transformations in industrial electrolyte:

$$2Cu^{2+} + 2TU = 2Cu^{+} + (NH_2)_2(NH)_2C_2S_2 + 2H^{+} \quad (4)$$

$$[Cu(FDS)]^{+} + e = Cu + FDS \quad (5)$$

**Table 3** Effect of thiourea concentration and temperature on diffusion coefficient of cupric ion in industrial electrolyte

| [thiourea]/ mg dm$^{-3}$ | $10^6$ D / cm$^2$s$^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 20°C | 30°C | 40°C | 50°C | 60°C |
| 0 | 4.75 | 6.87 | 9.37 | 14.0 | 17.9 |
| 1 | 5.26 | 7.43 | 6.68 | 9.55 | 18.2 |
| 2 | 5.75 | 6.87 | 9.48 | 9.40 | 13.6 |
| 3 | 5.91 | 7.10 | 9.95 | 13.2 | 15.2 |
| 4 | 5.15 | 6.60 | 9.40 | 14.0 | 16.0 |
| 5 | 5.65 | 7.46 | 10.4 | 14.5 | 20.4 |

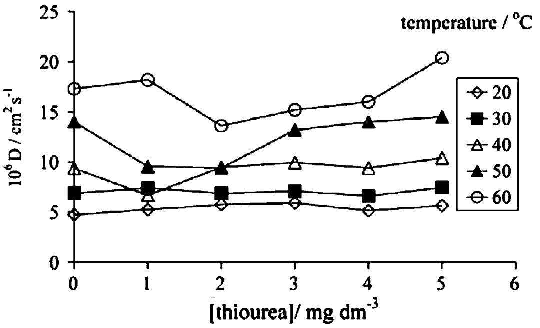

**Fig. 6** Diffusion coefficients as a function of thiourea concentration. Industrial electrolyte: 43.3 g dm$^{-3}$ Cu, without added animal glue

$$[Cu(TU)]^{+} + e = Cu + TU \quad (6)$$

$$[Cu(TU)]^{2+} + 2e = Cu + TU \quad (7)$$

$$FDS + 2e + 2H^{+} = 2TU \quad (8)$$

where *FDS* is formamidine disulphate.

These reactions prove the complexity of the transformations which thiourea undergoes in industrial electrolytes [19].

The results of this work show that the copper complexes presented above do not contribute substantially to the diffusion flux of copper ions to the cathode. This is a very important observation concerning the mechanism of copper electro-reduction in industrial solution.

## 4 Discussion and conclusions

The ultramicroelectrode [20] and chronoamperometry [20, 21] have been used previously in diffusion coefficient determination in synthetic industrial electrolytes, but copper ion concentrations were much lower than those used in electro-refining processes. Diffusion coefficients calculated in industrial electrolytes are lower in comparison to literature data concerning synthetic electrolytes under similar experimental conditions [2, 4]. The difference is due to the more complex composition of real industrial electrolytes. The diffusion coefficient calculated from electrochemical studies in industrial electrolyte (Cu 24.6 g dm$^{-3}$, ambient temperature) equals $4.22 \times 10^{-6}$ cm$^2$ s$^{-1}$ [22] and is close to the values obtained in this paper.

Increase in temperature increases the diffusion coefficient whilst increasing copper concentration causes a decrease. The latter result is expected since in concentrated solutions agglomerated diffusion coefficients should be calculated taking into account the concentration dependence of the activity coefficient of copper ions. Consequently, the variability of the apparent, experimental bulk diffusion coefficient is explained in terms of variability of activity coefficient as a function of copper concentration. The experimentally established diffusion coefficients are called apparent since they were determined assuming independence of diffusion coefficient on the electroactive species concentration, which is the case for relatively dilute electrolytes. As is clear from the results obtained in this work, in concentrated electrolytes (concentrations of copper ions varying from 0.3 to 1 mol $dm^{-3}$) the diffusion coefficient is dependent on copper ion concentration. Our results, obtained in concentrated electrolytes, cannot be explained using well known equations used in dilute/low concentrated electrolyte e.g. Nernst–Einstein equation.

According to the theory [23] the flux is defined by the following equation:

$$J_i = -\omega_i c_i \frac{d\mu_i}{dx} \tag{9}$$

where: $J_i$—flux of ions $i$, $\omega_i$—absolute mobility, $c_i$—concentration of ion $i$, $\mu_i$—electrochemical potential, $x$—distance from an electrode.

After taking into consideration the relation for electrochemical potential, the Eq. (9) is given by:

$$J_i = -\omega_i c_i RT \frac{1}{a_i}\frac{da_i}{dx} \tag{10}$$

where: $a_i$—ion activity.

In the case of concentrated solution studied in this work we cannot assume that activity is equal to concentration in the whole studied range of concentrations and consequently all dilute electrolytes relationships (where it is assumed that $a_i \approx c_i$) relationships are not strictly valid. The exact solution of the above equation requires knowledge of the relationship between activity (or its logarithm) and ionic strength of the solution. It is well known that this relationship is not linear at higher concentrations. Our experimental results concern systems which are still not as extensively studied as dilute electrolytes, either experimentally nor theoretically. This paper gives insight into the experimental parameters describing concentrated electrolytic solutions which are used in industrial electrorefining processes.

In the studied range of concentration, animal glue and thiourea modify the deposition of copper [24–25] rather than influence diffusion. This is a very important conclusion for industrial cathodic electroreduction of copper. It suggests that both agents influence the cathodic process mostly due to adsorption at the cathode surface. It is well known that thiourea can act as a ligand for copper ions but thiourea complex ion formation does not seem to significantly influence diffusion of copper ions at high concentrations.

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