



ELSEVIER

Journal of Electroanalytical Chemistry 501 (2001) 241–252

Journal of
Electroanalytical
Chemistry

www.elsevier.nl/locate/jelechem

The behaviour of copper anodes in aqueous thiourea-containing sulphuric acid solutions. Open circuit potentials and electrochemical kinetics

A.E. Bolzán*, I.B. Wakenge¹, R.C.V. Piatti, R.C. Salvarezza, A.J. Arvia*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA) (UNLP, CONICET, CICPBA), Facultad de Ciencias Exactas, Universidad Nacional de la Plata, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina*

Received 10 July 2000; received in revised form 14 September 2000; accepted 19 October 2000

Abstract

The electrochemical behaviour of copper anodes in aqueous thiourea (TU)-containing sulphuric acid was followed from open circuit potential measurements, voltammetry and rotating disk and ring-disk electrode data. The open circuit potential of copper is controlled by equilibria involving different Cu(I)–TU complex species. The thiourea electro-oxidation which yields formamidine disulphide and Cu(I)–TU complex species can be described as a process under intermediate kinetics taking place on a partially blocked copper anode. The degree of copper surface coverage and the type of predominant adsorbate depend on the concentration of thiourea and applied electric potential. Depending on the potential range adsorbates can be formed directly from either a strong TU–copper interaction or a relatively weaker formamidine disulphide interaction. The passivating layer can be related to the formation of polymer-like Cu(I)–TU layers and residues resulting both from thiourea and formamidine disulphide electro-oxidation. A previously proposed complex reaction pathway can explain the general behaviour of these systems, including adsorbate formation and the influence of the electrolyte solution constituents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper anodes; Thiourea adsorption; Copper electro-oxidation; Formamidine disulphide; Thiourea electro-oxidation

1. Introduction

A large number of publications have dealt with the effect of thiourea (TU) on both the electrocrystallisation and electrodisolution of copper in aqueous environments [1–10]. In the presence of TU, these processes become relatively complex by the concurrence of electrochemical reactions that are specific for TU, and chemical reactions between TU and copper ions [11]. The electro-oxidation of TU to formamidine disulphide, (H₂N)₂(HN)₂C₂S₂ (FDS), occurs at a potential lower than the threshold potential for copper electrodisolution in aqueous solutions [12]. Otherwise, FDS is also formed from the redox reaction between TU and Cu(II) ions in solution [13], yielding different

Cu(I)–TU complex ions such as [Cu_x(TU)_y]^{x+} cations, their stoichiometries depending on the Cu(II)–TU concentration ratio and the nature of anions present in the solution [14,15]. In fact, a number of Cu(I)–TU complexes have been recrystallised from acid copper sulphate and TU solutions [15]. Moreover, FDS is also capable of complexation and undergoes protonation [13]. In acidic solutions TU may undergo polycondensation to polythiourets, as concluded from the linear increase in polymer concentration with time and the reversibility of polymerisation [16].

A strong chemisorptive interaction of TU with copper has been concluded from electroreflectance spectra [16]. Recent STM imaging data of TU adsorbates on fcc metals such as Au(111) have shown that metal–TU interactions produce different potential-dependent adsorbate patterns with half-life times of the order of minutes [17]. At $E < E_{\text{Cu}^{\text{I}}-\text{Cu}^{\text{II}}}^{\text{r}}$, where $E_{\text{Cu}^{\text{I}}-\text{Cu}^{\text{II}}}^{\text{r}}$ is the reversible potential of the Cu(0)–Cu(II) redox couple in the solution, these adsorbates may exist either as proto-

* Corresponding author. Fax: + 54-221-4254642.

E-mail address: aebozlan@inifta.unlp.edu.ar (A.E. Bolzán).

¹ On leave from Université de Kinshasa, Faculté des Sciences, Département de Chimie, Kinshasa XI, République Démocratique du Congo.

nated TU, or as FDS or S adsorbed on copper [17]. Furthermore, a high degree of surface coverage by TU has been determined from open circuit potentials using the underpotential deposition of thallium as a test reaction [18]. At $E > E_{\text{Cu-Cu(II)}}^r$ it has been found that the electro-oxidation of TU and FDS yields a variety of products such as S- and CN-containing species, NH_4^+ , CO_2 and H_2SO_4 , their relative contributions depending on the experimental conditions [19].

This work reports reactions on polycrystalline copper electrodes in several aqueous TU- and FDS-containing 0.5 M sulphuric acid solutions, including open circuit potential (E_{oc}) measurements. For $E > E_{\text{oc}}$, the anodic reactions can be interpreted by a complex reaction pathway in which the electrochemistry of copper and the chemistry of TU in the presence of Cu(II) ions in the solution are considered. The proposed mechanism is useful for a better understanding of the influence of additives on copper corrosion inhibition and the role played by TU and its byproducts from electrochemical and chemical reactions in technical aqueous TU-containing copper plating baths.

2. Experimental

A number of experiments were made in a conventional glass-made three-electrode cell utilising electrorefined copper wires (diameter 0.5 mm, geometric area ca. 0.4 cm^2) as working electrodes. Each working

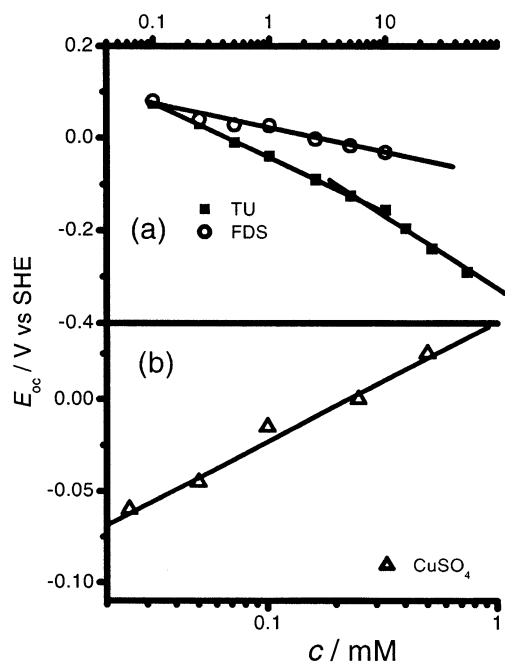


Fig. 1. (a) E_{oc} vs c_{TU} and E_{oc} vs c_{FDS} plots: (■) $x \text{ mM TU} + \text{aqueous } 0.5 \text{ M sulphuric acid}$; (○) $x \text{ mM FDS} + 0.5 \text{ M aqueous sulphuric acid}$; and (b) E_{oc} vs c_{CuSO_4} plot. $1 \text{ mM TU} + x \text{ mM copper sulphate} + \text{aqueous } 0.5 \text{ M sulphuric acid}$, 298 K.

electrode was first electropolished in aqueous concentrated phosphoric acid [20], and subsequently immersed in aqueous concentrated sulphuric acid for 60 s. This treatment provided a reproducible electrode surface.

Runs were also made using a rotating copper disk (RDE, type ED 10 K Tacussel) and a ring-disk (RRDE, type EAD 10 K Tacussel) electrode, consisting of a copper-disk/platinum-ring electrode 0.12 cm^2 in geometric area, and collection efficiency $N = 0.24$. The RDE and RRDE rotation speed (ω) was varied between 500 and 7000 rpm. Measurements were performed using a type BI-PAD Tacussel bipotentiostat.

In all cases, the counterelectrode was a large platinum sheet (2 cm^2 apparent area). Potentials (E) were measured against a saturated calomel electrode (SCE), although in the text they are given on the standard hydrogen electrode (SHE) scale.

Working solutions were prepared from Fluka, puriss. p.a. chemicals, 97% Merck, p.a. sulphuric acid and Milli-Q* water. They were kept under nitrogen saturation before and during the experiment.

The influence of TU, FDS, copper ions in solution and pH on the copper electrode open circuit potential (E_{oc}) was determined using the following solutions: aqueous 0.5 M sulphuric acid + $x \text{ mM TU}$ ($0.1 \leq x \leq 50$); 0.5 M sulphuric acid + 1 mM TU + $x \text{ mM copper sulphate}$ ($0 \leq x \leq 0.5$); 0.5 M sulphuric acid + $x \text{ mM FDS}$ ($0.1 \leq x \leq 10$); 0.5 M sulphuric acid + 1 mM TU + $x \text{ mM FDS}$ ($0.1 \leq x \leq 10$); $x \text{ M sulphuric acid} + (0.5 - x) \text{ M sodium sulphate} + 1 \text{ mM TU}$; $x \text{ M sulphuric acid} + (0.5 - x) \text{ M sodium sulphate} + 1 \text{ mM FDS}$ and $x \text{ M sulphuric acid} + (0.5 - x) \text{ M sodium sulphate} + 0.1 \text{ mM copper sulphate}$. As reported in the text, values of E_{oc} were stable for at least 30 min.

Conventional voltammetry was run with either aqueous TU- or FDS-containing 0.5 M sulphuric acid utilising a conventional potentiostat and waveform generator.

All runs were made at 298 K.

3. Results

3.1. Open circuit potentials

In the range $0.1 \text{ mM} \leq c_{\text{TU}} \leq 50 \text{ mM}$, the value of E_{oc} for copper in aqueous TU-containing 0.5 M sulphuric acid decreases as the concentration of TU (c_{TU}) is increased. The E_{oc} vs $\log c_{\text{TU}}$ plot shows two linear regions with slopes approaching $-0.118 \pm 0.005 \text{ V decade}^{-1}$ for $0.1 \text{ mM} \leq c_{\text{TU}} \leq 10 \text{ mM}$, and $-0.180 \pm 0.005 \text{ V decade}^{-1}$ for $10 \text{ mM} \leq c_{\text{TU}} \leq 50 \text{ mM}$ (Fig. 1a). The crossing point lies at $E_{\text{oc}} \approx -0.17 \text{ V}$ and $c_{\text{TU}} \approx 6 \text{ mM}$.

As FDS participates in those equilibria related to the TU-copper system [1], it was worth establishing the

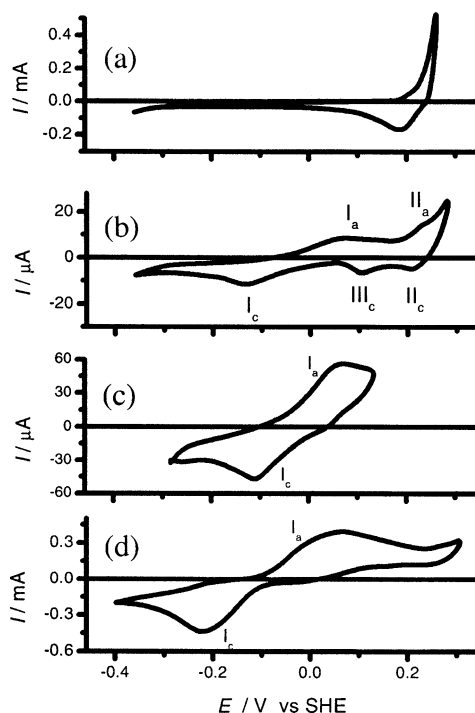


Fig. 2. Cyclic voltammograms for copper in aqueous 0.5 M sulphuric acid with different concentrations of TU: (a) 0 mM; (b) 0.5 mM; (c) 1 mM; (d) 10 mM, $v = 0.05 \text{ V s}^{-1}$ at 298 K.

influence of c_{FDS} on E_{oc} both in the presence and absence of TU. For copper in aqueous FDS-containing 0.5 M sulphuric acid, the value of E_{oc} decreases linearly with $\log c_{\text{FDS}}$. The slope of this line approaches $-0.059 \text{ V decade}^{-1}$ for $0.1 \text{ mM} \leq c_{\text{FDS}} \leq 10 \text{ mM}$. For $c_{\text{FDS}} > 10 \text{ mM}$, the determination of open circuit potentials is limited by the solubility of FDS in the acid solution. It should be noted that for $c_{\text{TU}} \approx c_{\text{FDS}} < 0.02 \text{ mM}$, both E_{oc} vs $\log c_{\text{TU}}$ and E_{oc} vs $\log c_{\text{FDS}}$ linear plots tend to coincide. Otherwise, for copper in 1 mM TU + x mM FDS ($0.1 \leq x \leq 10$) + 0.5 M sulphuric acid, the value of E_{oc} remains practically constant. These results show that the value of E_{oc} for copper immersed in these solutions is determined by the presence of TU, irrespective of the presence of FDS in the solution. This fact strongly suggests that the Cu–TU interaction becomes stronger than the Cu–FDS interactions, in agreement with energy calculations made for the metal surface–thiol and the metal surface–dithiol [21].

In copper sulphate ($0.025 \text{ mM} \leq c_{\text{CuSO}_4} \leq 0.5 \text{ mM}$) + 1 mM TU + aqueous 0.5 M sulphuric acid, E_{oc} increases almost linearly with $\log c_{\text{CuSO}_4}$. The slope of the straight line is $0.060 \pm 0.005 \text{ V decade}^{-1}$ (Fig. 1b). Finally, the value of E_{oc} becomes pH-independent in the range $0.9 \leq \text{pH} \leq 5.8$ for both TU- and FDS-containing solutions. This dependence of E_{oc} on the solution composition can be analysed considering those chemical reactions and equilibria in which aqueous Cu(I)–TU complex species are involved [22], as is

discussed later. The stoichiometry of these complex species depends on the composition of the solution, particularly on the initial Cu(II)–TU molar concentration ratio [14,15].

3.2. Cyclic voltammetry

Cyclic voltammograms of copper in aqueous TU-containing 0.5 M sulphuric acid run at $v = 0.05 \text{ V s}^{-1}$ (Fig. 2a) from -0.35 to 0.26 V exhibit a flat current profile, with an increasing anodic faradaic current starting from ca. 0.19 V in the positive direction due to the commencement of copper electrodisolution. This process involves a first positive hump related to the $\text{Cu}(0) \rightleftharpoons \text{Cu}(\text{I}) + e^-$ reaction and a second abrupt increase in anodic current due to the $\text{Cu}(0) \rightleftharpoons \text{Cu}(\text{II}) + 2e^-$ overall reaction. The subsequent reverse scan shows a negative peak at ca. 0.19 V due to the electrodeposition of Cu(II) ions formed in the preceding potential scan. This process is associated with the cathodic current plateau that extends in the range $0.05 \text{ V} \leq E \leq -0.25 \text{ V}$. Finally, starting from -0.25 V in the negative direction, the cathodic current increases steadily due to the contribution of the hydrogen evolution reaction (her) on copper.

For copper in aqueous 0.5 mM TU + 0.5 M sulphuric acid the cyclic voltammogram run at 0.05 V s^{-1} between -0.35 and 0.28 V (Fig. 2b) exhibits two positive (I_{a} and II_{a}) and three negative (I_{c} , II_{c} and III_{c}) current peaks. Conjugated peaks I_{a} and I_{c} are more clearly defined by potential scanning between -0.3 and 0.15 V , at 0.01 V s^{-1} , in 1 mM TU + 0.5 M sulphuric acid (Fig. 2c). The pair of peaks II_{a} and II_{c} appears to be related to a second conjugated electrochemical reaction. Peak III_{a} which can be correlated to that observed in aqueous TU-free 0.5 M sulphuric acid (Fig. 2a), corresponds to copper electrodeposition from a very low concentration of Cu(II) ions remaining in the solution after copper electro-oxidation has occurred. As c_{TU} is increased to 10 mM, peaks I_{a} and II_{c} are strongly depressed, whereas peak III_{c} is no longer observed. In this case, an anodic current plateau covering the range 0.1 – 0.25 V is recorded (Fig. 2d).

The heights of peaks I_{a} , II_{c} and III_{c} depend linearly on $v^{1/2}$ (Fig. 3). Otherwise, no clearcut linear dependence of peak potentials ($E_{\text{p,a}}$ and $E_{\text{p,c}}$) on either v or $\log v$ was observed, as expected for a simple, either reversible or irreversible, electrochemical reaction under diffusion control [23].

The value of the $I_{\text{p,a}}$, (the height of peak I_{a}) vs $v^{1/2}$ plot, at constant c_{TU} , approaches a linear relationship only for $v < 0.01 \text{ V s}^{-1}$, whereas an increasing deviation from the linearity expected for a simple diffusion controlled electrochemical reaction [23] is found for $v > 0.1 \text{ V s}^{-1}$ (Fig. 4). From these plots, it also results that the $I_{\text{p,a}}/I_{\text{p,a}}'$ ratio from cyclic voltammograms,

where $I_{p,a}^1$ is the value of $I_{p,a}$ read from the linear plot, is independent of v . These facts suggest that on increasing c_{TU} an accumulation of adsorbed TU residues on the copper anode is produced, which would lead to a decrease in the effective area of the copper anode. Therefore, the deviation of the $I_p/v^{1/2}$ plot from linearity could be assigned to a surface blockage by TU and

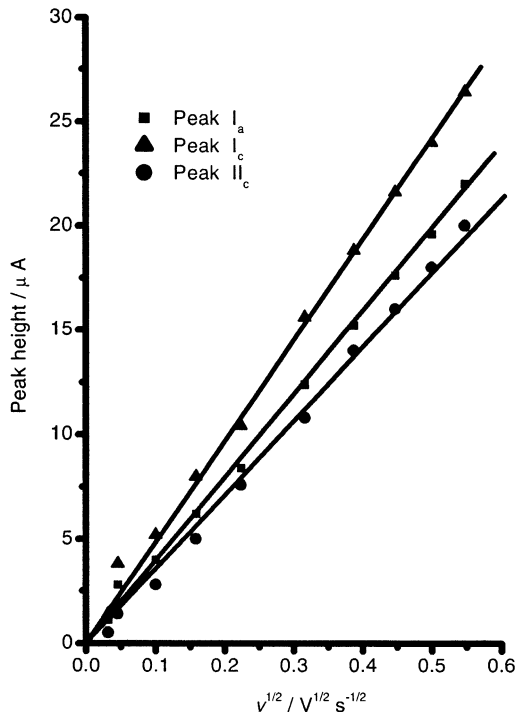


Fig. 3. Voltammetric peak heights vs $v^{1/2}$ plots; 0.5 mM TU + aqueous 0.5 M sulphuric acid, 298 K.

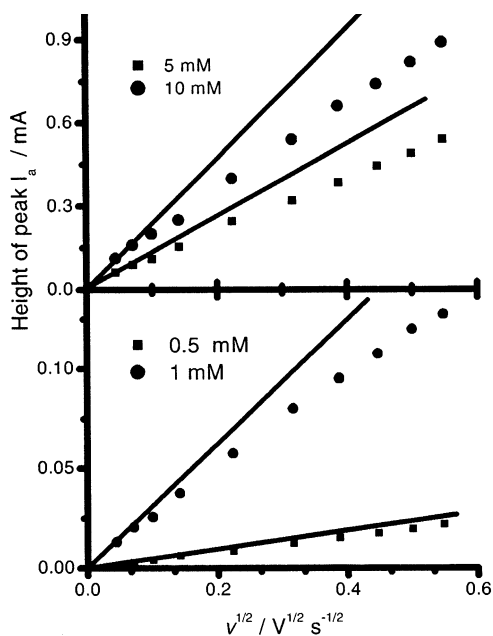


Fig. 4. Height of peak I_a vs $v^{1/2}$ plots for different c_{TU} ; x mM TU + aqueous 0.5 M sulphuric acid, 298 K.

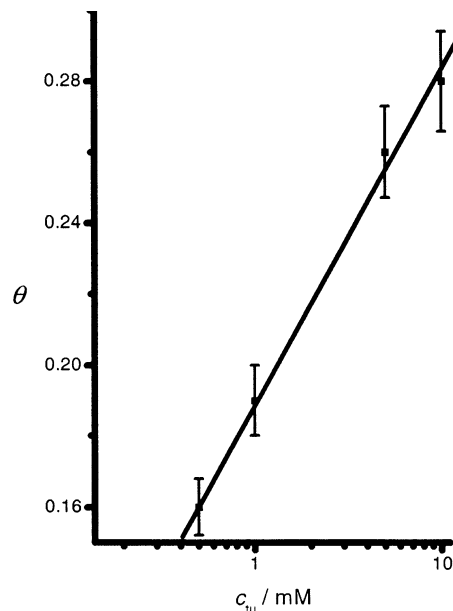


Fig. 5. Plot of θ vs $\log c_{TU}$ resulting from cyclic voltammetry run at $v = 0.15 \text{ V s}^{-1}$ (Fig. 4).

TU-derivative adsorbates. Accordingly, the degree of surface coverage (θ) by adsorbates can be estimated as $\theta = 1 - I_{p,a}/I_{p,a}^1$, the value of θ increasing linearly with $\log c_{TU}$ (Fig. 5).

3.3. Adsorbate formation from TU on copper

The formation of TU adsorbates on copper has been demonstrated by several procedures [16,18,24–26]. These adsorbates play a definite role in the electrochemical reactions of copper in aqueous TU-containing solutions.

The presence of TU adsorbates on copper, as well as their electro-oxidation potential window, was confirmed by the underpotential deposition (upd) of thallium on copper as a test reaction. A blank voltammogram for copper in aqueous 0.1 mM thallium sulphate + 0.5 M sulphuric acid (Fig. 6) run from 0 V in the negative direction, i.e. in the potential range where alloying effects are negligible [27–30], exhibits a negative hump at ca. -0.32 V related to thallium upd. This hump overlaps, to some extent, the cathodic current baseline related to the her, whereas in the reverse scan, a well-defined single positive peak at ca. -0.25 V , due to the anodic stripping of thallium, can be observed. The charge density resulting from the positive peak is 0.15 mC cm^{-2} , a figure which is about one-half of that expected for 1.5 monolayers of thallium [29]. It has been demonstrated that this charge density depends on whether the copper surface has been subjected to a mechanical or an electropolishing electrode pretreatment [29]. Correspondingly, either single or multiple peaks for thallium upd on copper are observed [18].

Otherwise, when the copper electrode has been previously immersed in aqueous 0.5 mM TU + 0.5 M sulphuric acid for 30 s at $E = -0.35$ V, the subsequent voltammogram in 0.1 mM thallium sulphate + 0.5 M sulphuric acid shows a strong decrease both in thallium up and anodic stripping charges. After deconvolution from the contribution of her the thallium stripping charge is 0.02 mC cm^{-2} . Accordingly, from the charge

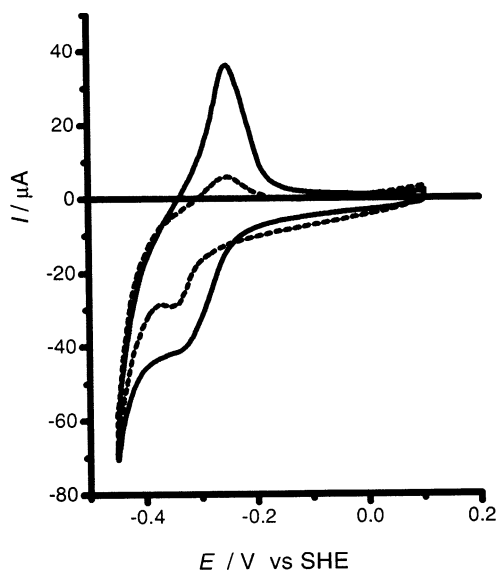


Fig. 6. Voltammograms of copper in aqueous 0.1 mM thallium sulphate + 0.5 M sulphuric acid; blank (full trace). After immersion at -0.45 V for 30 s in 0.5 mM TU + aqueous 0.5 M sulphuric acid (dotted trace). Electrode area 0.4 cm^2 , $v = 0.05 \text{ V s}^{-1}$ at 298 K.

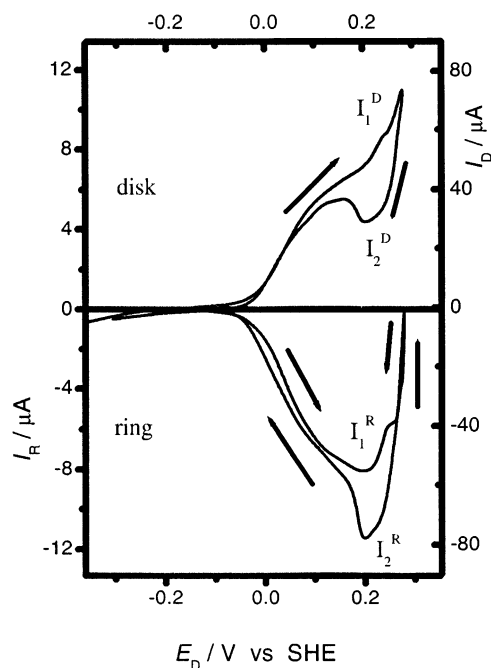


Fig. 7. Rotating ring disk voltammograms; 0.5 mM TU + aqueous 0.5 M sulphuric acid. $E_R = -0.26$ V; $\omega = 2000$ rpm; $v = 0.05 \text{ V s}^{-1}$ at 298 K.

ratio of this experiment and that of the blank, the copper surface coverage by TU adsorbates was estimated as 85%, a figure which is comparable to that found for TU adsorbates on Au(111) from STM imaging [17].

Finally, the voltammogram of TU adsorbates on copper run in aqueous 0.5 M sulphuric acid between -0.3 and 0.17 V, i.e. a potential window between the her and the copper electrodisolution threshold potential, showed no electro-oxidation current attributable to TU adsorbates. Therefore, it appears that TU adsorbates on copper are essentially stable at potentials below the TU electro-oxidation threshold potential.

3.4. RRDE data

Rotating ring-disk current/potential profiles in aqueous 0.5 mM TU + 0.5 M sulphuric acid run in the positive potential direction between -0.36 and 0.28 V at $v = 0.05 \text{ V s}^{-1}$ and $\omega = 2000$ rpm (Fig. 7), show a very small current both at the copper disk and platinum ring electrodes. The anodic current at the disk approaches a quasi-limiting value at 0.15 V. At ca. 0.2 V, the anodic current rises again showing up a small hump (I_1^D) at ca. 0.24 V. The reverse potential scan shows a remarkable hysteresis, i.e. first the current decreases to a minimum value at ca. 0.2 V (I_2^D), and then it increases up to a maximum. Later, the current tends to overlap the positive-going potential voltammetric scan. These results suggest that in the range $0 \text{ V} \leq E_D \leq 0.2 \text{ V}$ mass transfer and surface electrochemical reactions are involved. It should be noted that for $c_{\text{TU}} = 0.5 \text{ mM}$, the decrease in v from 0.05 to 0.005 V s^{-1} produces a strong decrease of both I_1^D and I_2^D . Simultaneously, the cathodic current at the ring held at $E_R = -0.26$ V increases steadily. Subsequently, a small wave is observed and finally, the null current is attained. The reverse scan first shows a cathodic current jump followed by the appearance of peak I_2^R , and when $E_D \approx -0.1$ V, the current decreases to zero.

Data from RRDE experiments depend on v , ω and c_{TU} . Thus, as c_{TU} is increased from 0.5 to 10 mM and v is decreased from 0.05 to 0.005 V s^{-1} , the disk voltammogram in the positive potential direction shows no peaks such as those described above for $c_{\text{TU}} = 0.5 \text{ mM}$; the overall voltammogram displays an anodic current plateau with a hysteresis loop (Fig. 8). Likewise, the cathodic current at the ring held at $E_R = -0.26$ V exhibits a remarkable hysteresis with a current maximum at ca. 0.12 V. For the reverse potential scan, the cathodic current at the ring decreases almost linearly with E_D .

These results are consistent with the formation of soluble products that are electroreduced at the platinum ring held at $E_R = -0.26$ V during the electro-oxidation of TU at the copper disk electrode. The formation of

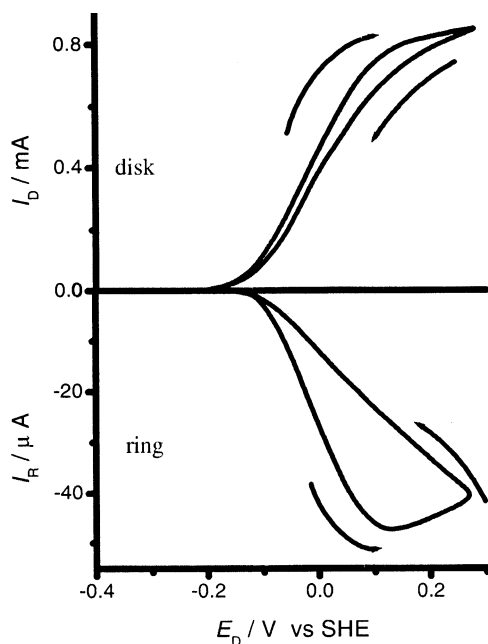


Fig. 8. Rotating ring disk voltammograms; 10 mM TU + aqueous 0.5 M sulphuric acid. $E_R = -0.26$ V; $\omega = 2000$ rpm; $v = 0.005$ V s $^{-1}$.

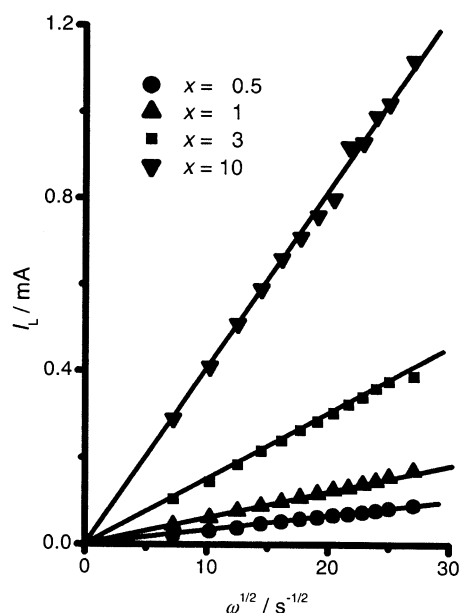


Fig. 9. Plots of I_L vs $\omega^{1/2}$ derived from quasi-stationary current potential curves recorded at $v = 0.005$ V s $^{-1}$ in x mM TU + aqueous 0.5 M sulphuric acid at 298 K.

soluble products appears to be gradually inhibited as $E_D > 0.2$ V, i.e. in the potential range where the electrodisolution of copper to Cu(II) ions in the blank is observed (Fig. 2). This inhibition is likely caused by the accumulation of insoluble Cu(I) complex species at the electrode/solution interface [18,31], although the effect tends to disappear as either c_{TU} is increased or v is decreased, i.e. when an excess of TU is present at the

reaction interface the passivating film that is formed on the anode tends to dissolve.

3.5. RDE data

For a copper RDE immersed in aqueous x mM TU + 0.5 M sulphuric acid the anodic limiting current (I_L), recorded at $v = 0.005$ V s $^{-1}$, changes linearly with $\omega^{1/2}$ (Fig. 9). The slope from these plots, $\Delta I_L / \Delta \omega^{1/2}$, increases with c_{TU} (Fig. 10), although this increase is slower than that expected from a $\Delta I_L / \Delta \omega^{1/2}$ vs c_{TU} linear dependence. This behaviour is consistent with that already described from the voltammetric current peaks on c_{TU} (Fig. 4). It suggests that the mass transport-controlled anodic reaction is to some extent hindered by a progressive blockage of the electrode surface by reaction products, as c_{TU} is increased.

The deviation from linearity of the $\Delta I_L / \Delta \omega^{1/2}$ vs c_{TU} plot (Fig. 10) can be related to an increase in the value of θ with c_{TU} . Following the same assumption made for voltammetric data, for quasi-steady adsorption conditions prevailing at the RDE, values of θ were obtained from the deviation of the above-mentioned plot. In this case, the result is again that θ approaches a linear increase with $\log c_{TU}$ (Fig. 10, inset). At constant c_{TU} , the difference in the values of θ in the plots depicted in Figs. 5 and 10 (inset) is coherent with the specific conditions of each type of experiment.

The quasi-stationary current/potential curves covering the potential range 0 V $\leq E_D \leq -0.2$ V fit the Koutecky–Levich-like plots (Fig. 11). The slope of these linear plots is almost independent of c_{TU} , as

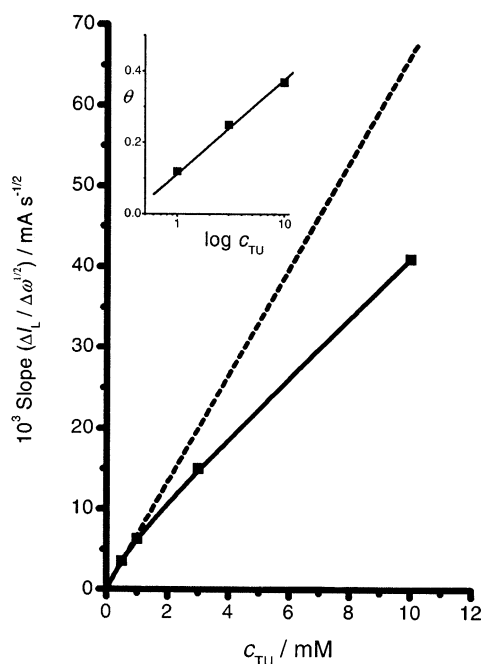


Fig. 10. Plots of $\Delta I_L / \Delta \omega^{1/2}$ vs c_{TU} and θ vs $\log c_{TU}$. Data derived from Fig. 9.

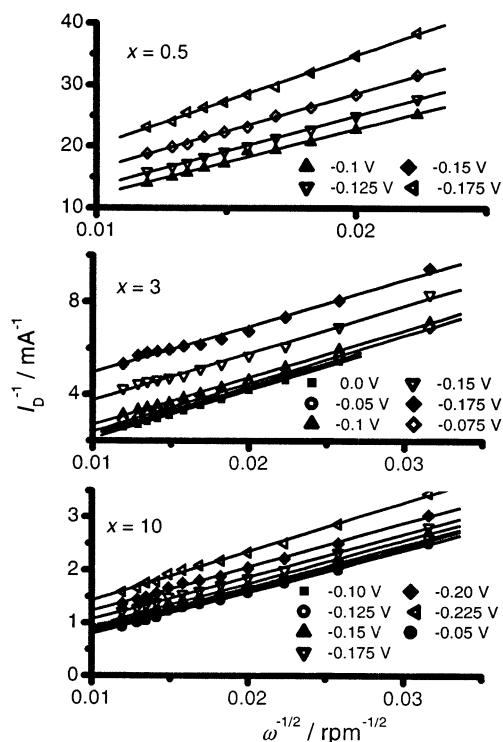


Fig. 11. Plots of $1/I$ vs $1/\omega^{1/2}$ at different E derived from quasi-stationary curves recorded at 0.005 V s^{-1} in $x \text{ mM TU} + \text{aqueous } 0.5 \text{ M sulphuric acid}$ at 298 K .

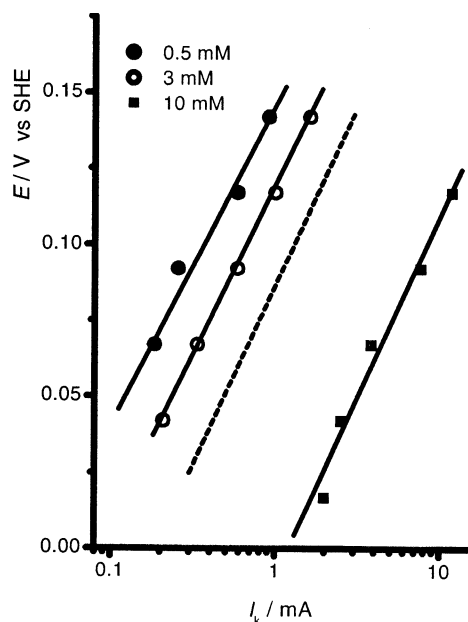


Fig. 12. Plots of I_k vs E for copper in $x \text{ mM TU} + \text{aqueous } 0.5 \text{ M sulphuric acid}$. Dotted line indicates the slope $0.118 \text{ V decade}^{-1}$.

expected for a first-order electrochemical reaction under mass transport control. The value of the ordinate for $\omega \rightarrow \infty$ provides the true kinetic current I_k for the heterogeneous electrochemical reaction. The value of I_k

fits a reasonable E_D vs $\log I_k$ linear relationship with a slope $b_T = \Delta E_D / \Delta \log I_k \approx 0.118 \text{ V decade}^{-1}$ (Fig. 12).

4. Discussion

The electrochemistry of copper in aqueous TU-containing acid solution becomes more complex than previously thought [18], particularly because only in recent years has the knowledge of these systems been enriched by the advances in the understanding of nature of ionic complexes and structures of compounds produced and recrystallised from solutions [14,15], and the stability and structure of TU and TU-derivatives adlayers [17]. In fact, the formation of rather stable complexes in aqueous TU- and Cu(II)-containing acid solutions involves a number of chemical reactions and homogeneous and heterogeneous equilibria, and TU-copper and TU-derivatives-copper interactions that play an important role in dealing with both anodic and cathodic copper electrode reactions in these solutions. Therefore, for such systems, it is convenient to first review the most relevant chemical and electrochemical reactions that might be of interest for the interpretation of data presented in this work.

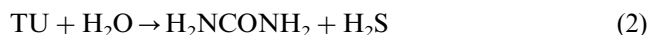
4.1. Chemistry of aqueous TU-containing acid solutions

It is well known that TU is a fairly large polarisable molecule, most likely poorly solvated in aqueous solutions, and that it exhibits acid-base properties [32]. In highly acid solutions, TU exists predominantly as a monoprotonated species $\text{NH}_2\text{CSNH}_3^+$ [33]



with a protonation constant of 1.44 at 298 K [34]. In aqueous 0.5 M sulphuric acid, the fraction of protonated TU is about 2–4% [35].

Conversely, the hydrolysis of TU in aqueous solution yields urea and hydrogen sulphide [36]



Reaction (2) being favoured by the tautomeric form $\text{H}_2\text{NHNC-SH}$ [19].

In acidic solutions the chemical oxidation of TU and its alkyl derivatives with hydrogen peroxide yields a mixture of ammonia, sulphur, sulphuric acid and carbon dioxide [37]. This complex process might be of interest for the electrochemical reactions on metals in aqueous TU-containing electrolyte solutions [25,38,39].

As occurs for thiols [40], in acid aqueous solutions TU and FDS are involved in the redox process reaction [12]



where the standard potential of Reaction (3) is $E^0 = 0.420$ V (SHE) [1,41]. Reaction (3) is favoured by the deprotonation of the tautomeric form of TU.

The stabilisation of FDS depends on the electrolyte composition; FDS can be crystallised in the form of either a chlorhydrate or a sulphate. The spontaneous decomposition of FDS in acid yields different products: TU, cyanamide and sulphur being the most important [42,43]. This process, which is also interesting for those reactions occurring at high positive potentials [18], can be followed by the absorption bands in the visible–UV spectra for TU at 237 nm and for FDS at 206 nm [13].

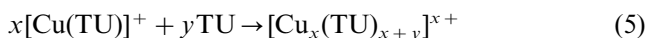
4.2. Chemistry of TU in Cu(II)-containing solutions

In aqueous Cu(II) and TU-containing solutions, TU is oxidised by Cu(II) ions [44] yielding FDS and Cu(I)–TU complex species [13] through a formal reaction such as



where $[\text{Cu}(\text{TU})]^+$ represents a primary complex ion in solution without stoichiometric specification. It has been reported that reaction (4) exhibits a polarographic anodic–cathodic wave near 0.242 V (SHE) [12]. The positive charge of the ionised complex has been determined using the Hittorf method [13] and its absorption spectrum characterised by a band at 340 nm [13]. The chemical reduction of Cu(II) ions by TU in solution can be followed by UV–vis spectrophotometry [45].

Although the complex ion yielded by Reaction (4) has been described as $[\text{Cu}(\text{TU})]^+$ ($\log \beta_4 = 15$ [46]), several stable forms of Cu(I)–TU complex ions with a number of TU ligands higher than 1 were also proposed earlier [47] and later observed [14,15]. In this case, primary complex ions from reaction (4) would react further as follows:



Reaction (5) applies to different stable complex species whose stoichiometry depends on the concentration ratio between Cu(II) ions and TU in solution. The structure and stoichiometry of sulphate salts containing one of the $[\text{Cu}_4\text{TU}_7]^{4+}$, $[\text{Cu}_4\text{TU}_6]^{4+}$, $[\text{Cu}_2\text{TU}_5]^{2+}$ or $[\text{Cu}_2\text{TU}_6]^{2+}$ cations were recently determined by X-ray diffractometry [14,15]. The formation of these complexes has been explained from the typical chemical behaviour of the thiol form of thioamides, such as TU, which permits its oxidation to disulphide. In contrast to N-substituted derivatives that are capable of complexing metal ions in their higher oxidation state such as Cu(II), because thiol–thione tautomerism is impeded, unsubstituted thioureas form only Cu(I) complexes [48].

From the standpoint of surface chemistry, during the electrodeposition of Cu(II) it has been proposed that Cu(I) ions form adsorbed complexes with TU at low

current densities, whereas at high densities adsorption saturation with respect to TU is attained, then the discharge from Cu(II) aquo complex ions takes place [47].

Finally, in Cu(II)-containing solutions neither FDS nor its decomposition products form those complex species that are characterised by an absorption band at 340 nm [13].

4.3. System copper–TU adsorbates

Radiotracer and electroreflectance (ER) data [16] of copper in aqueous TU-containing 1.5 M sulphuric acid have shown a strong chemisorptive interaction of TU with copper without sulfur formation, as the counting of ^{14}C did not decrease. For $c_{\text{TU}} < 1$ mM, the coverage of copper by TU increases slowly to reach a monolayer coverage as the potential approaches 0.2 V [16]. Conversely, for $c_{\text{TU}} > 1$ mM, the surface coverage increases sharply with E up to the multilayer level, although no adsorption equilibrium is attained for $E > -0.2$ V. Seemingly, TU undergoes polycondensation to polythiourets, as concluded from the linear increase in polymer concentration with time and the reversibility of the polymerisation process [16]. The adsorption of TU on copper from aqueous TU-containing 1 M perchloric acid attains a maximum coverage at ca. 0.1 V [24].

As has been concluded from SERS data, TU adsorbs onto copper via the S atom [25]. This is favoured by the $\text{H}_2\text{NHNC-SH}$ tautomeric form of TU [19]. The shift of the corresponding spectral bands due to the presence of TU species agrees with the formation of Cu(I) complexes involving TU and sulphate at the electrode surface [25].

In situ IR spectra of the copper–TU adsorbate/solution interface taken at potentials negative to E_{oc} provided evidence of the partial desorption of TU from copper in 0.5 M sulphuric acid. Changes exhibited by N–C–N bipolar symmetric vibrational bands were assigned to either a protonation of the S atom or to adsorption of TU via the S atom [26].

Finally, in the potential range where the electrodisolution of copper takes place, TU and FDS decompose yielding adsorbed sulphur-containing and other residual species that promote the localised electrodisolution of copper [18].

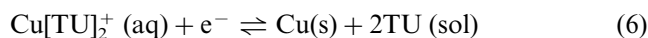
4.4. Open circuit potential of copper electrodes in aqueous 0.5 M sulphuric acid

4.4.1. Thiourea-containing solutions

For copper in aqueous $0.1 \text{ mM} \leq c_{\text{TU}} \leq 10 \text{ mM} + 0.5$ M sulphuric acid, the slope of the E_{oc} vs $\log c_{\text{TU}}$ plot (Fig. 1a) is close to -0.118 V decade $^{-1}$. This linear portion extends over the range $-0.16 \text{ V} \leq E_{\text{oc}} \leq 0.08$ V, i.e. the potential window where the pair of peaks

I_a/I_c is observed (Fig. 2). This coincidence, however, cannot be explained by reaction (3), as the latter would predict the slope -0.059 V decade $^{-1}$. Therefore, it seems reasonable to relate the behaviour of these values of E_{oc} to the presence of Cu(I)–TU complexes.

Thus, considering the simplest equilibrium reaction, in which copper and TU are involved



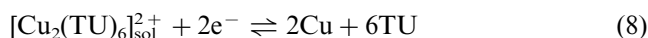
the corresponding Nernst equation, at 298 K, is

$$E = E^0 - 0.059 \log \frac{[\text{TU}]^2}{[\text{Cu}(\text{TU})_2]^+} \quad (7)$$

where E^0 stands for the standard potential including activity coefficients, brackets refer to the concentration of reactants and products, and $a_{\text{Cu}} = 1$.

Eq. (7) predicts an E_{oc} vs $\log c_{\text{TU}}$ linear dependence with the slope -0.118 V with respect to c_{TU} and a linear E_{oc} vs $\log c_{[\text{Cu}(\text{TU})_2]^+}$ plot with the slope 0.059 V decade $^{-1}$, in agreement with experimental data for $c_{\text{TU}} < 10$ mM (Fig. 1). The structure of the $\text{Cu}(\text{TU})_2^+$ complex as the chloride salt has been determined by X-ray diffractometry [49].

On the other hand, for $c_{\text{TU}} > 10$ mM, the increase in $\Delta E_{oc}/\Delta \log c_{\text{TU}}$ to -0.180 V decade $^{-1}$ can be assigned to an increase in the number of TU molecules participating in a complex reaction such as Reaction (6). In fact, the presence of Cu(I)–TU complexes of different stoichiometries offers an alternative for interpreting the E_{oc} vs $\log c_{\text{TU}}$ plots [15]. For instance, considering that the $[\text{Cu}_2\text{TU}_6]^{2+}$ species is formed from solutions containing Cu(II) ions and an excess of TU ($c_{\text{TU}} \gg 10$ mM) [15], then the following reaction:



whose equilibrium potential is given by the equation

$$E = E^0 - \frac{0.059}{2} \log \frac{[\text{TU}]^6}{[\text{Cu}_2(\text{TU})_6]^{2+}} \quad (9)$$

accounts for the slope -0.180 V derived from the linear E vs $\log c_{\text{TU}}$ plot (Fig. 1). It should be pointed out that the $[\text{Cu}_2\text{TU}_6]^{2+}$ species has also been identified and its structure determined by X-ray diffractometry [15].

4.4.2. TU- and copper sulphate-containing solutions

When Cu(II) ions are added to x mM TU + 0.5 M sulphuric acid solution and the condition $c_{\text{CuSO}_4} \ll c_{\text{TU}}$ is fulfilled, Cu(II) ions react with TU according to reaction (4), i.e. almost all Cu(II) ions are reduced to Cu(I)–TU complexes. Assuming that the simple stoichiometry shown in Eq. (6) is valid and that $c_{\text{TU}} = c_{\text{CuSO}_4}$, a linear E_{oc} vs $\log c_{\text{CuSO}_4}$ plot with the slope -0.059 V decade $^{-1}$ is obtained, in agreement with the slope observed from this type of solution (Fig. 1b).

4.4.3. FDS-containing solutions

The value of E_{oc} in 1 mM TU + x mM FDS + aqueous 0.5 M sulphuric acid remains constant irrespective of c_{FDS} . Otherwise, in the absence of TU, the value $\Delta E_{oc}/\Delta \log c_{\text{FDS}} = -0.059$ V decade $^{-1}$ is consistent with the equilibrium



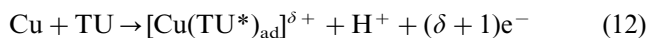
the Nernst equation being

$$E = E^0 - 0.059 \log \frac{[\text{FDS}]}{[\text{Cu}(\text{FDS})]^+} \quad (11)$$

It should be noted that reactions (6), (8) and (10) do not depend on the solution pH, in agreement with the experimental data, at least for the range $0.9 \leq \text{pH} \leq 5.8$.

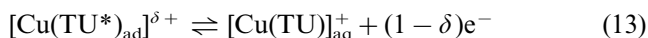
4.5. Kinetics and possible reaction pathway for copper electro-oxidation in TU-containing sulphuric acid solutions

The first stage for the electro-oxidation of TU on copper involves the adsorption of TU on the metal via its tautomeric form [19], TU-adsorbates being produced at either constant potential or open circuit condition, reaching a surface coverage of ca. 80% after 300 s, as concluded from thallium upd experiments (Fig. 6). The TU adsorption process presumably involves a partial charge transfer similar to that found for the adsorption of thiols on gold [50]



yielding a fractional monolayer coverage by TU^* , where TU^* stands for a deprotonated TU molecule. This reaction is supported by recent quantum calculations that showed that the adsorption energy for the S–H form of TU is much lower than that obtained for the =C=S form [21].

As was concluded previously [12,13,44,46,51], in the range $0.14 \text{ V} \leq E \leq 0.17 \text{ V}$, Reaction (12) favours the electro-dissolution of copper to Cu(I) according to a reaction that can be formally written as



Then, $\text{Cu}(\text{TU}^*)_{\text{ad}}$ can be considered as a precursor of copper electro-dissolution through $[\text{Cu}(\text{TU})_{\text{aq}}]^+$ species yielding soluble Cu(I) complex ions in solution.

Otherwise, in the potential range $0.14 \text{ V} \leq E \leq 0.17 \text{ V}$ (Fig. 2) the electro-oxidation of TU on copper yields soluble FDS (peak I_a) from either the electro-oxidation of adsorbed TU or the radical ion $\text{TU}^{+\cdot}$ in solution [52], whereas the electro-reduction of soluble FDS to TU is related to peak I_a . In principle, the linear dependence of both peaks I_a and I_c on $v^{1/2}$ at a constant c_{TU} and the difference $\Delta E_p = E_{p,a} - E_{p,c} = 0.2$ V, a figure greater than 0.059 V, indicates that these reactions involve the

diffusion of reactants from the bulk of the solution to the electrode surface with a considerable degree of irreversibility [23], as is discussed later.

The soluble FDS produced by the electro-oxidation of TU can also be adsorbed on the copper electrode. The formation of adsorbed FDS has been observed on Au(111) by in situ STM imaging [17], although the interaction of FDS with metal surfaces is expected to be weaker than that of TU, as has been earlier concluded from the comparative adsorption of thiols and disulphides on gold [53,54]. The formation of FDS also assists the electro-dissolution of copper presumably through the formation of an intermediate such as $\text{Cu}(\text{FDS})_{\text{ad}}$ [18]. A possible reaction pathway for these processes has been discussed recently [18].

The hump I_1^{P} and peaks I_2^{D} , observed at the RDE for $E_{\text{D}} \approx 0.2$ V (Fig. 7), are related to a surface adsorption process involving FDS superimposed onto the mass transport controlled TU electro-oxidation and copper electro-dissolution currents. The contribution of this surface process is influenced by both c_{TU} and v , i.e. as c_{TU} is increased or v is decreased, the current contributions I_1^{P} and I_2^{D} tend to disappear (Fig. 8). This would mean that surface species related to these current contributions are gradually suppressed by increasing either c_{TU} or the reaction time (decreasing v), i.e. under favourable conditions for a chemical reaction between surface species and TU.

On the other hand, the potentials at which hump I_1^{P} and peak I_2^{D} in the RRDE are observed, are close to the Cu(II)–Cu(I) equilibrium potential [11]. The anodic charges related to these current contributions are 0.042 mC cm^{-2} for hump I_1^{P} and 0.092 mC cm^{-2} for peak I_2^{D} . Hump I_1^{P} can be assigned to the formation of the insoluble polymer-like film from adsorbed TU-species [31]. This film hinders the formation of soluble anodic products, as seen by the RRDE response (Fig. 7) and favours the formation of soluble Cu(II) ions at the reaction interface, as seen from the enhancement of cathodic current at the ring, and the appearance of peak I_2^{D} at the disk, which corresponds to the electroreduction of a part of Cu(II) remaining at the reaction interface which is captured at relatively high v and low c_{TU} .

It should be noted that the contribution of sulphide species to the appearance of peaks I_1^{P} and I_2^{D} was ruled out because the addition of small amounts of sodium sulphide to the TU-containing solutions had no significant effect on the voltammetric runs.

Finally, for $E > 0.2$ V, FDS is oxidised to S- and CN-containing species [18], a process that eventually changes the nature of products blocking the copper surface.

4.6. Kinetic parameters for TU electrochemical reactions at copper electrodes in aqueous TU-containing 0.5 M sulphuric acid

At constant c_{TU} , the dependence of peak I_{a} on $v^{1/2}$ deviates from linearity on increasing v (Fig. 4). This behaviour can be interpreted assuming a partial blockage of the anode surface which interferes with the mass transfer process. This interference can be accounted for by considering an effective electrode area (A_{ef}), which can be expressed as $A_{\text{ef}} = A_0(1 - \theta)$, where A_0 is the geometric electrode area, and θ is a c_{TU} - and potential-dependent surface coverage by adsorbates. Values of θ can be obtained from either data shown in Fig. (5) or from the deviation of the slopes of the plots of $\Delta I_{\text{L}}/\Delta \omega^{1/2}$ with c_{TU} (Fig. 10, inset). Accordingly, TU electro-oxidation on copper in aqueous sulphuric acid can be described as an electrochemical reaction under intermediate kinetics on an electrode surface which is progressively blocked as c_{TU} is increased. This also makes the reverse reaction more irreversible as manifested by the hysteresis loop in the RDE polarisation curves (Fig. 8), and the $\Delta E_{\text{p}} \approx 0.2$ V in the voltammograms.

As far as TU adsorbates on copper is concerned, the θ vs $\log c_{\text{TU}}$ dependence resulting from different experiments (Figs. 5 and 10, inset) suggests that the adsorption is influenced by the surface heterogeneity as predicted by the Temkin adsorption model [55].

At constant c_{TU} , the dependence of the quasi-steady limiting current (I_{L}) on $\omega^{1/2}$ fulfils the Levich equation

$$I_{\text{L}} = 0.620nFA_{\text{ef}}D_{\text{i}}^{2/3}v^{-1/6}c_{\text{TU}}\omega^{1/2} \quad (14)$$

where n is the number of electrons per reactant molecule, F is the Faraday constant and ν is the kinematic viscosity of the solution. Eq. (14) is fulfilled over the whole range of c_{TU} used in the present work (Fig. 9). Considering $A_{\text{ef}} = A_0(1 - \theta)$, values of θ shown in Fig. 10 (inset), $n = 1$ and $\nu \approx 0.01 \text{ cm}^2 \text{ s}^{-1}$, it results in $D_{\text{i}} = 9 \pm 0.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the different values of c_{TU} . This figure for D_{i} agrees with that recently reported for TU electro-oxidation on platinum electrodes [38] and with the values 1.2×10^{-5} and $8.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ that have been reported for TU on copper electrodes in nitric [56] and sulphuric acid [57] solutions, respectively.

The linearity of the Koutecky–Levich-like plots in the mixed kinetic regime (Fig. 11) is consistent with a first-order electrochemical reaction [23] as in the case of the electro-oxidation of TU on platinum electrodes [38]. The overall current involves the contribution of I_{k} , the true kinetic current that can be derived from these plots at different potentials. Values of I_{k} fulfil a Tafel relationship with the slope $b_{\text{T}} \approx 0.118 \text{ V decade}^{-1}$ (Fig. 12), i.e. a figure which is consistent with the first single electron transfer as the rate determining step [58].

On the other hand, I_{k} can be expressed as

$$I_k = nFA_{\text{cr}}c_{\text{TU}}k^0 \exp(\alpha nFE/RT) \quad (15)$$

where k^0 is the standard heterogeneous rate constant and α is the transfer coefficient assisting the reaction in the positive direction.

Therefore, from the $\log I_k$ vs E plots, for the different c_{TU} , we find that in $k^0 = 5 \pm 3 \times 10^{-3} \text{ cm s}^{-1}$ and $\alpha = 0.55 \pm 0.03$. The value of k^0 is about one order of magnitude higher than that found for platinum electrodes [38], in agreement with the lower value of ΔE_p resulting from the voltammograms (Fig. 2) as compared to that recorded for platinum (ca. 0.45 V). It should be noted that the value of k^0 does not have a universal meaning due to the complex characteristics of the reacting surface.

5. Conclusions

- The dependence of the open circuit potential of copper in aqueous TU-containing 0.5 M sulphuric acid on the concentration of TU can be explained by the formation of several TU–Cu(I) complexes of different stoichiometries. The value of E_{oc} depends neither on the pH ($0.9 \leq \text{pH} \leq 5.8$) nor on the FDS concentration ($0.1 \text{ mM} \leq c_{\text{FDS}} \leq 10 \text{ mM}$) in solution.
- In the low potential range, the electro-oxidation of TU on copper yields FDS and Cu(I) complex ions, these reactions being accompanied by the formation of TU and TU derivatives on the copper surface, which act as precursors of copper electrodisolution.
- Depending on the potential range, adsorbates are formed either directly from a strong TU–copper interaction or from a weaker FDS–copper interaction. Insoluble polymer-like TU–Cu(I) layers are formed.
- Kinetic data can be interpreted as a first-order single electron transfer under a mixed regime. The Levich equation is obeyed provided that a correction term for the effective electrode area is considered. This correction can be made from the analysis of either voltammetric or RDE data.
- A complex reaction pathway, which has been proposed previously, accounts for the electrochemical behaviour of TU and FDS on copper electrodes in aqueous TU-containing sulphuric acid. It involves the participation of different adsorbates and Cu(I) complex ions in solution. These conclusions are useful to understand the effect of sulphur-containing additives on metal electrode reactions.

Acknowledgements

This work was supported financially by the Consejo Nacional de Investigaciones Científicas y Técnicas

(CONICET) (PIP 4376) and Agencia Nacional de Promoción Científica y Tecnológica (PICT 98 06-03251) of Argentina and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC). B.I.W. thanks the Third World Academy of Science (TWAS) and CONICET for the fellowship granted.

References

- [1] D. Suarez, F. Olson, *J. Appl. Electrochem.* 22 (1992) 1002.
- [2] E.E. Farndon, F.C. Walsh, S.A. Campbell, *J. Appl. Electrochem.* 25 (1995) 574.
- [3] V.S. Martín, S. Sanlloriente, S. Palmiero, *Electrochim. Acta* 44 (1998) 579.
- [4] A.C. Makrides, N. Hackerman, *Ind. Engng Chem.* 47 (1955) 1773.
- [5] M.J. Jannssen, *Spectrochim. Acta* 17 (1961) 474.
- [6] T.K. Ross, D.H. Jones, *J. Appl. Chem.* 12 (1962) 314.
- [7] K.C. Pillai, R. Narayan, *J. Electrochem. Soc.* 125 (1978) 1393.
- [8] B.C. Ateya, B.E. El-Anadoul, F.M. El-Nizamy, *Corros. Sci.* 24 (1984) 497.
- [9] R. Agarwal, T.K.G. Nambodhiri, *Corros. Sci.* 30 (1990) 37.
- [10] Z.D. Stankovic, M. Vukovic, *Electrochim. Acta* 41 (1996) 2529.
- [11] U. Bertocci, D.R. Turner, in: A.J. Bard (Ed.), *Encyclopedia of Electrochemistry of the Elements*, vol. II, Marcel Dekker, New York, 1974 (Ch. VI).
- [12] A. Szymaszek, J. Biernat, L. Pajdowski, *Electrochim. Acta* 22 (1977) 359.
- [13] P. Javet, H.E. Hintermann, *Electrochim. Acta* 14 (1969) 527.
- [14] R.C. Bott, G.A. Bowmaker, C.A. Davis, G.A. Hope, B.E. Jones, *Inorg. Chem.* 37 (1998) 651.
- [15] O. Piro, R.C.V. Piatti, A.E. Bolzán, R.C. Salvarezza, A.Y. Arvia, *Acta Crystallogr. B* 56 (2000) 493.
- [16] G.V. Korshin, A. Petukhov, A.M. Kuznetsov, Y.M. Vyzhimov, *Elektrokhimiya* 27 (1991) 275.
- [17] O. Azzaroni, B. Blum, R.C. Salvarezza, A.J. Arvia, *J. Phys. Chem. B Lett.* 104 (2000) 1395.
- [18] A.E. Bolzán, A.S.M.A. Haseeb, P.L. Schilardi, R.C.V. Piatti, R.C. Salvarezza, A.J. Arvia, *J. Electroanal. Chem.* (2001), in press.
- [19] E.E. Reid, *Organic Chemistry of Bivalent Sulfur*, vol. 5, Chemical Publishing, 1963.
- [20] P. Shigolev, *Electrolytic and Chemical Polishing of Metals*, Freund Publishing House, Tel Aviv, 1974.
- [21] P. Carro, private communication.
- [22] J. Biernat, A. Szymaszek, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 24 (1976) 133.
- [23] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- [24] G. Horanyi, E.M. Rizmayer, P. Joó, *J. Electroanal. Chem.* 149 (1983) 221.
- [25] C.M. Brown, C.A. Hope, D.P. Schweinsberg, P.M. Fredericks, *J. Electroanal. Chem.* 380 (1995) 161.
- [26] D. Papapanayiotou, R.N. Nuzzo, R.C. Alkire, *J. Electrochem. Soc.* 145 (1998) 3366.
- [27] D.M. Kolb, in: H. Gerischer, G. Tobias (Eds.), *Advances in Electrochemistry and Electrochemical Engineering*, vol. 11, Wiley, New York, 1978.
- [28] R.R. Adzic, *Israel J. Chem.* 18 (1979) 166.
- [29] D.A. Berg, D.S. Nadezdhim, R.G. Barradas, *J. Electroanal. Chem.* 355 (1993) 165.
- [30] A. Hernández Creus, R.M. Souto, S. González, M.M. Laz, R.C. Salvarezza, A.J. Arvia, *Appl. Surf. Sci.* 81 (1994) 387.
- [31] A.S.M.A. Haseeb, P.L. Schilardi, R.C.V. Piatti, A.E. Bolzán, R.C. Salvarezza, A.J. Arvia, *J. Electroanal. Chem.* 500 (2001) 533–542.

- [32] M. Hoffmann, J.O. Edwards, *Inorg. Chem.* 16 (1977) 3333.
- [33] G. Davies, *Inorg. Chem.* 11 (1972) 2489.
- [34] V.P. Vasil'ev, V.I. Shorokhova, N.K. Grechina, L.V. Katrovtsseva, *Russ. J. Inorg. Chem.* 23 (1978) 1274.
- [35] J.H. Barber, B.E. Conway, *J. Chem. Soc. Faraday Trans.* 92 (1996) 3709.
- [36] D.R. Turner, G.R. Johnson, *J. Electrochem. Soc.* 109 (1962) 382.
- [37] H. Marshall, *Proc. R. Soc. Edinburgh* 24 (1902) 233.
- [38] A.E. Bolzán, I.B. Wakenge, R.C. Salvarezza, A.J. Arvia, *J. Electroanal. Chem.* 475 (1999) 181.
- [39] M. Yan, K. Liu, Z. Jiang, *J. Electroanal. Chem.* 408 (1996) 225.
- [40] D.S. Tarbell, in: N. Kharasch (Ed.), *Organic Sulfur Compounds*, vol. 1, Pergamon, New York, 1961 (Ch. X).
- [41] P.W. Preisler, L. Berger, *J. Am. Chem. Soc.* 69 (1947) 322.
- [42] E.A. Werner, *J. Chem. Soc.* 101 (1912) 2166.
- [43] F. Kurzer, P.M. Sanderson, *J. Chem. Soc.* (1959) 1058.
- [44] H.M. Ratajczak, L. Pajdowski, *Inorg. Nucl. Chem.* 36 (1974) 431.
- [45] P. Schilardi, A.E. Bolzán, R.C.V. Piatti, O.E. Piro, C. Gutiérrez, R.C. Salvarezza, A.J. Arvia, in preparation.
- [46] E.I. Onstott, H.A. Laitinen, *J. Am. Chem. Soc.* 72 (1950) 4724.
- [47] N. Zukauskaitė, A. Malinauskas, *Electrokhimiya* 24 (1988) 1567.
- [48] P. Caston, J. Jaud, N.P. Johnson, R. Soules, *J. Am. Chem. Soc.* 107 (1985) 5011.
- [49] W.A. Spofford, E.L. Hamma, *Acta Crystallogr. B* 26 (1970) 1474.
- [50] D.W. Hatchett, K.J. Stevenson, W.B. Lacy, J.M. Harris, H.S. White, *J. Am. Chem. Soc.* 119 (1997) 6596.
- [51] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, Chichester, 1980.
- [52] S.J.J. Reddy, V.N. Krishnan, *J. Electroanal. Chem.* 27 (1970) 473.
- [53] L.-H. Wan, Y. Hara, H. Noda, M. Osawa, *J. Phys. Chem. B* 102 (1998) 5943.
- [54] T.Y. Leung, M.C. Gerstenberg, D.J. Lavrich, G. Scoles, F. Schreiber, G.E. Porter, *Langmuir* 16 (2000) 549.
- [55] A.W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 1982.
- [56] J. Kirchnerová, W.C. Purdy, *Anal. Chim. Acta* 123 (1981) 83.
- [57] M. Alodan, W. Smyrl, *Electrochim. Acta* 44 (1998) 299.
- [58] B.E. Conway, *Theory and Principles of Electrode Kinetics*, Ronald Press, New York, 1965.