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# Voltammetric characterization of laprol 2402 C adsorption on copper and tin electrodes

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Voltammetric investigation of Cu(II) and Sn(II) reduction was carried out in sulphate solutions containing laprol 2402C as a surface-active substance. No pronounced effect was detected in Cu|Cu(II) system at laprol concentration ( $c_{\text{lap}}$ ) ranging up to 10 mg dm<sup>-3</sup>.

Only a slight increase in overvoltage was observed in the region of low cathodic polarizations at  $c_{\text{lap}} = 100$  mg dm<sup>-3</sup>. On the contrary, a strong inhibitive adsorption was found to occur in Sn|Sn(II) system. A simplified model involving the Temkin isotherm gives a satisfactory agreement between the experimental and simulated current densities in the region of voltammogram plateau. Characteristic minima were found to develop on the voltammograms obtained for Cu(II), Sn(II) and laprol containing solutions. Adsorption layers resulting in strong inhibition seem to be formed of laprol and products of Sn(II) reduction.

**Key words:** copper, tin, codeposition, laprol, adsorption

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## INTRODUCTION

Investigations aimed for developing plating baths allowing to obtain bronze coatings of high quality are of considerable interest. Since the difference between the standard potentials of Cu|Cu(II) and Sn|Sn(II) electrodes is significant (*ca* 0.5 V), optimal conditions for Cu and Sn codeposition may be achieved using special additives such as ligands and/or surface-active substances (SAS). Various polyethers may be mentioned among the latter group of additives.

Bronze plating bath containing laprol 2402C (product of polycondensation of ethene and propene oxides with average molecular mass of 3200) has been developed and introduced into plating industry [1]. Some data on voltammetric characteristics of the process reported in [2] showed a strong influence of laprol on partial processes.

Similar SAS have been investigated in different systems [3–14]. An inhibitive behaviour of polyethylene glycol (PEG) in Cu/Cu(II) system was described 20 years ago [8]. According to [9], two adsorption states of PEG on Cu electrode are possible: 1 nm thick layer containing Cu<sup>2+</sup>, PEG and Cl<sup>-</sup> forms at equilibrium potential and exhibits a strong inhibition. The latter effect has not been found to occur at higher cathodic polarizations where adsorption of neutral PEG was suggested.

Comprehensive reviews concerning the influence of PEG on Cu(II) reduction were reported by Stoychev [10, 11]. It has been stated that the adsorption of this substance may be strong or weak depending on the electrode polarization and solution composition. Polymer molecules may lose their electroneutrality due to formation of complexes with Cu<sup>+</sup> or Cu<sup>2+</sup>. Chloride anions enhance the PEG adsorption.

An inhibitive adsorption of similar SAS is also known for tin and its alloys [2, 12–14]. For instance, adsorption of syntanol DS-10 decreases tenfold the double layer capacitance of Sn electrode [14].

Since literature data concerning the adsorption behaviour of laprol are few in number, we made an attempt to fill some gaps in this problem. This paper deals with voltammetric study of laprol adsorption on copper and tin as components of bronze coatings.

## EXPERIMENTAL

Triply distilled water, CuSO<sub>4</sub> · 5H<sub>2</sub>O, SnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> (analytical grade) were used to prepare solutions. Laprol 2402C with the average molecular mass 3200 was used as received. The concentration of Cu(II) and Sn(II) was controlled by complexometric and iodometric titration, respectively. Deaeration of solutions was carried out by pure argon by passing

the stream through the solution before measurements for 0.5 h and over solutions when the curves were recorded.

5  $\mu\text{m}$  thick copper or tin coatings deposited on Pt substrate served as working electrodes. The following solutions were used for this purpose ( $\text{g dm}^{-3}$ ):  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  200,  $\text{H}_2\text{SO}_4$  – 50 (for Cu deposition) and  $\text{SnSO}_4$  – 50,  $\text{H}_2\text{SO}_4$  – 160, laprol – 1 (for Sn deposition).

A saturated  $\text{Ag}|\text{AgCl}$ ,  $\text{KCl}$  electrode served as reference. To protect the working solutions from  $\text{Cl}^-$  ions, chloride-free electrolytic junction was used and changed after each experiment. All potential values were transformed to the hydrogen scale.

A conventional rotating disc technique was used with a  $5 \text{ mV s}^{-1}$  potential scan rate. All experiments were performed at  $20^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Electrodeposition of copper

The voltammograms obtained under forced convection conditions for SAS-free solutions are shown in Fig. 1 by solid lines. An equilibrium potential ( $E_{\text{eq}}$ ) of  $\text{Cu}|\text{Cu(II)}$  electrode resulting from Nernst equation at  $\gamma = 0.07$  [15] was calculated to be equal to 0.245 V. Experimentally observed open-circuit potentials ( $E_{\text{oc}}$ ) are in good ( $\pm 2 \text{ mV}$ ) agreement with above the  $E_{\text{eq}}$  value. Some irregularities of the voltammograms were found to occur in the vicinity of  $-0.1 \text{ V}$  for the solutions which were reliably protected from  $\text{Cl}^-$  ions (see Experimental). This effect

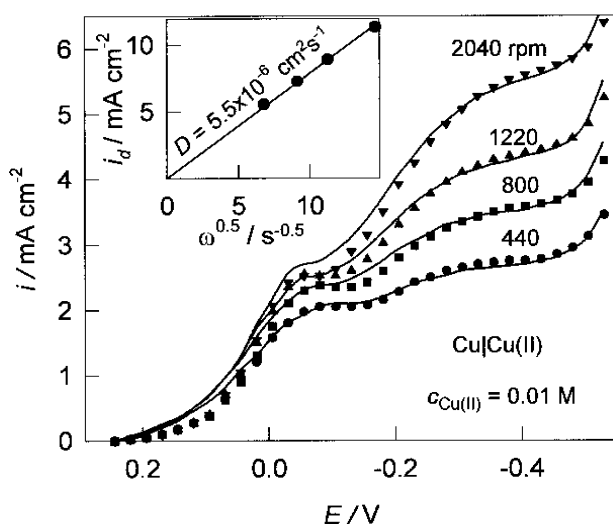


Fig. 1. Voltammograms of  $\text{Cu(II)}$  reduction obtained for  $0.01 \text{ M Cu(II)}$  solutions at different rotating velocities of  $\underline{rde}$  indicated on the curves (rpm). Levich plot of current density determined at  $-0.45 \text{ V}$  is given in the inset. Data for laprol-free solutions and for those with  $c_{\text{lap}} = 100 \text{ mg dm}^{-3}$  are displayed by full lines and symbols respectively

seems to be conditioned by consecutive charge transfer and needs a special analysis. A plateau of limiting current density ( $i_d$ ) observed at sufficiently high overvoltages follows Levich equation (see inset in Fig. 1), which yields the diffusion coefficient of  $\text{Cu}^{2+}$  ions  $D = 5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

Addition of laprol up to  $c_{\text{lap}} = 100 \text{ mg dm}^{-3}$  exerts no detectable effect on  $E_{\text{oc}}$ , which remains unchanged within the limits of experimental error. The same statement is valid for entire voltammograms at  $c_{\text{lap}} \leq 10 \text{ mg dm}^{-3}$ . Only a comparatively high amount of the SAS ( $100 \text{ mg dm}^{-3}$ ) produces some changes in the voltammetric behaviour of the system (symbols in Fig. 1). The main effect is observed at low cathodic overvoltages ( $0 < E < 0.245 \text{ V}$ ) and manifests itself in a moderate shift of electrode potential towards more negative values. A similar effect was found to occur in solutions containing polyethylene glycol [8]. The results obtained suggest that laprol has no pronounced effect on the kinetics of  $\text{Cu(II)}$  reduction in chloride-free solutions.

### Electrodeposition of tin

The open-circuit potential of  $\text{Sn}|\text{Sn(II)}$  electrode ( $-0.24 \text{ V}$ ) in SAS-free solutions is consistent with  $E_{\text{eq}}$  at  $\gamma \approx 0.5$ . Voltammograms (Fig. 2) flatten out at lower cathodic polarizations as compared to the similar data obtained for  $\text{Cu}|\text{Cu(II)}$  electrode (Fig. 1). This suggests that the equilibrium charge exchange process at  $\text{Sn}|\text{Sn(II)}$  interface is more rapid.

As in the case of Cu electrode,  $i_d$  also follows Levich equation (see inset in Fig. 2), which yields

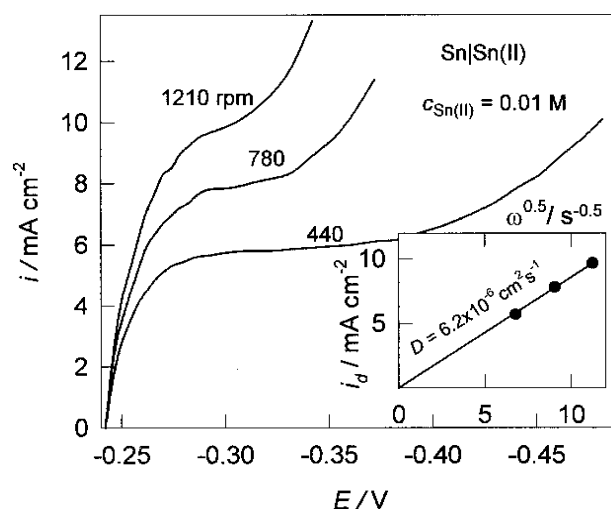


Fig. 2. Voltammograms of  $\text{Sn(II)}$  reduction obtained for  $0.01 \text{ M Sn(II)}$  solutions at different rotating velocities of  $\underline{rde}$  indicated on the curves. Levich plot of current density determined at  $-0.3 \text{ V}$  is given in the inset

$D = 6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . However, the influence of laprol is quite different. An inhibition of Sn(II) reduction takes effect even at a very low  $c_{\text{lap}}$  and approaches the limit at  $ca \text{ } 100 \text{ mg dm}^{-3}$  (Fig. 3). At the same time the system ceases to obey the regularities of diffusive mass transport. If a certain effect of forced convection intensity can be revealed at  $c_{\text{lap}} = 0.5 \text{ mg dm}^{-3}$ , this is not the case at  $c_{\text{lap}} = 10 \text{ mg dm}^{-3}$  (Fig. 4). All these data are indicative of strong inhibitive adsorption of laprol on the Sn electrode. The adsorption layers affect not only the partial process of Sn(II) reduction, but also the evolution of hydrogen increasing its overvoltage.

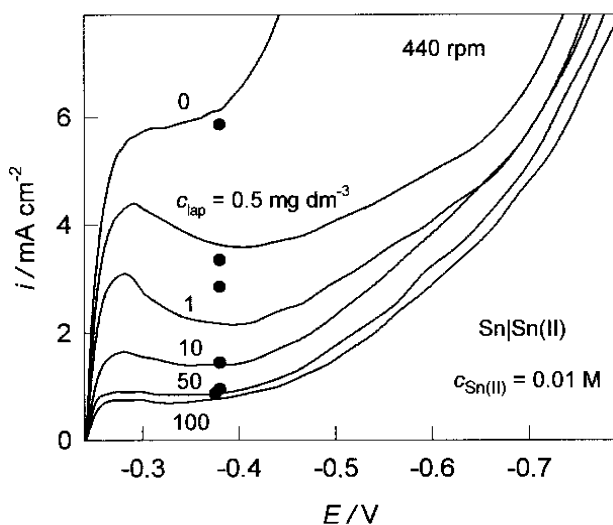


Fig. 3. Effect of laprol on voltammograms obtained for 0.01 M Sn(II) solutions at 440 rpm. Laprol concentrations are indicated on the curves. Simulated  $i$  values (see Table 1) are shown by symbols

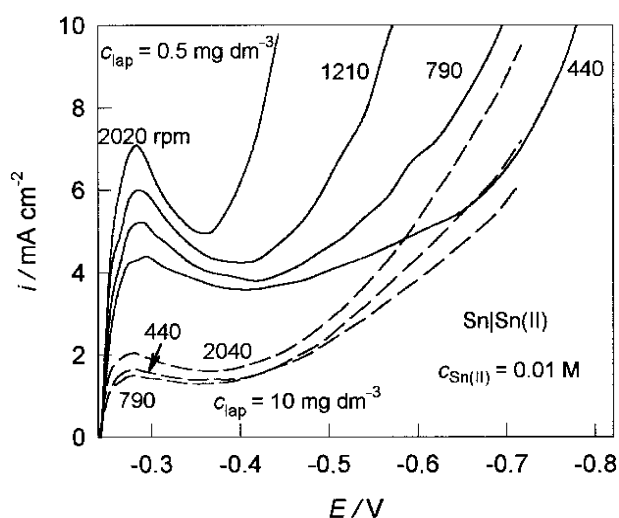


Fig. 4. Effect of forced convection intensity on voltammograms obtained for 0.01 M Sn(II) solutions containing  $0.5 \text{ mg dm}^{-3}$  (full lines) and  $10 \text{ mg dm}^{-3}$  (dotted lines) of laprol

To account for the influence of laprol adsorption on Sn(II) reduction rate, a simplified model was used as follows. Let us assume that the current density may be described by the relationship

$$i = i_{\theta=0}(1 - \theta) + i_{\theta=1} \theta \quad (1)$$

where  $\theta$  is the surface coverage,  $i_{\theta=0}$  and  $i_{\theta=1}$  are current densities at  $c_{\text{lap}} = 0$  and  $c_{\text{lap}} \rightarrow \infty$ , respectively. The latter quantity may be obtained by the extrapolation procedure. Thus, the  $\theta$  values may be calculated from experimental data (Fig. 3) at a constant potential. To determine a relation between  $c_{\text{lap}}$  and  $\theta$ , a certain adsorption isotherm should be used. According to [16], a simplified Temkin isotherm was found to give the best results for the systems containing some polyethers. We used this isotherm as given in [17]:

$$Bc = \frac{\exp(a\theta) - 1}{1 - \exp[-a(1 - \theta)]}, \quad (2)$$

where  $B$  is a potential-dependent adsorption constant,  $a$  is a parameter accounting for an interaction between adsorbed particles. A fitting procedure was applied to the experimental data obtained for  $E \approx -0.4 \text{ V}$  (Fig. 3) with  $i_{\theta=0} = 5.86$  and  $i_{\theta=1} = 0.76 \text{ mA cm}^{-2}$ . The best fit was obtained at  $B = 50.30 \text{ mg}^{-1} \text{ dm}^3$  and  $a = 6.558$ . The data listed in Table show a satisfactory agreement between the simulated and the experimental data.

Table. Results of fitting procedure				
$c_{\text{lap}}$ $\text{mg dm}^{-3}$	$\theta$		$i$ , $\text{mA cm}^{-2}$	
	Eqn. (1)	Fit	Exp.	Fit
0	0	0	5.86	5.86
0.5	0.45	0.49	3.57	3.35
1	0.72	0.59	2.16	2.85
10	0.86	0.87	1.45	1.44
50	0.96	0.96	0.96	0.95
100	0.98	0.98	0.86	0.86

### Codeposition of copper and tin

Some experimental data relating the solutions containing both Cu(II) and Sn(II) have been reported previously [2]. A deep well-defined minimum of current density has been found to develop at certain potentials. According to [18, 19], instability phenomena prevailing in the region of the negative slope of a voltammogram give rise to current oscillations. A closer examination of the solutions shows that a rather small amount of Sn(II) is sufficient to originate the minimum under discussion (Fig. 5). The onset of current decrease occurs at a potential which

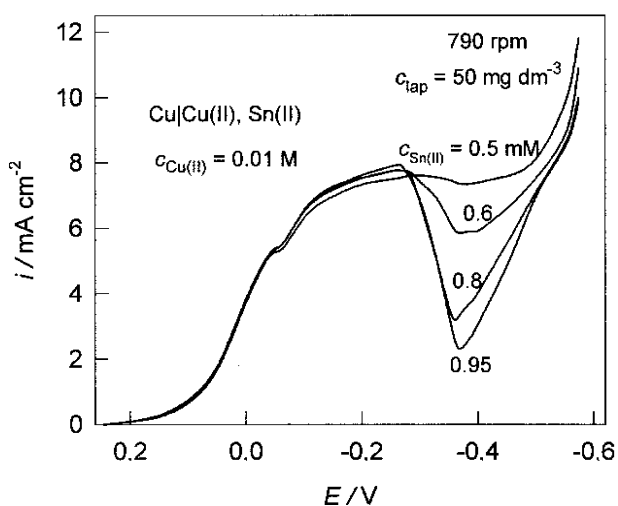


Fig. 5. Voltammograms obtained at 790 rpm for Cu electrodes in solutions containing 0.01 M of Cu(II), 50 mg dm<sup>-3</sup> of laprol and different amounts of Sn(II) indicated on the curves

is close to  $E_{eq}$  of Sn|Sn(II) couple. This means that electroreduction of Sn(II) is probable at this point.

Some optional data are available from Fig. 6 where the influence of forced convection is also shown. Voltammograms may be arbitrarily subdivided into two parts. At  $E > -0.28$  V, they actually coincide for different  $c_{Sn(II)}$  and  $c_{lap}$  but differ from voltammetric data obtained for Sn(II) – free solutions (cf. Figs. 1, 5 and 6). The mechanism of such behaviour is not yet clear. On the contrary, both Sn(II) and laprol retard the net electrochemical process at a more negative  $E$ . As can be seen from Figs. 5 and 6, the depth of the minimum strongly depends on Sn(II) concentration.

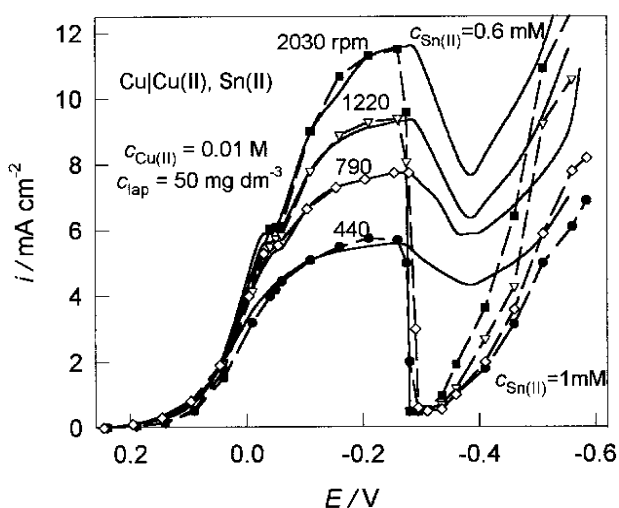


Fig. 6. Voltammograms obtained for Cu electrodes in solutions containing 0.01 M of Cu(II), 50 mg dm<sup>-3</sup> of laprol and 0.6 mM (full lines) or 1 mM (symbols and dotted lines) of Sn(II).  $R_{de}$  rotating velocity (rpm) is indicated on the curves

Let us consider, for instance, data for a solution containing 1 mM of Sn(II) and 50 mg dm<sup>-3</sup> of laprol (Fig. 6). A sharp current decrease takes less than 5 s at  $E \approx -0.28$  V. According to Figs. 3 and 4, the partial current density of Sn(II) reduction ( $I_{Sn}$ ) is ca 1 mA cm<sup>-2</sup> for  $c_{Sn(II)} = 0.01$  M. Assuming that  $I_{Sn}$  varies linearly with  $c_{Sn(II)}$ , we have a charge of ca 0.5 mC which may be employed for Sn(II) reduction. The further estimation shows that the amount of Sn(II) to be deposited should be less than one monolayer.

According to the results obtained, the top inhibition of the electrochemical process is attained at  $c_{Sn(II)} \approx 1$  mM. Laprol contains  $-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2-$  and  $-\text{CH}_2-\text{O}-\text{CH}_2-$  chains with the average molecular mass of ca 50. This means that 1 mM of such chain exists in the solution under discussion. It follows further that the ratio of oxygen and Sn<sup>2+</sup> is 1:1 when the state of inhibition saturation is achieved.

Polymers similar to laprol are known to form complexes with Cu<sup>2+</sup> and Cu<sup>+</sup> [10, 11]. It is not unreasonable to suggest that Sn<sup>2+</sup>-laprol complexes may be also formed. Then the adsorption layer resulting in strong inhibition might be considered as a product of full or partial reduction of the above complexes. It might contain Sn ad-atoms or Sn<sup>+</sup> adions. The possibility of formation of Sn<sup>+</sup> intermediate has been reported in [20]. More definite conclusions on the composition of adsorption layers are not available from the presented data. This problem needs further investigation.

## CONCLUSIONS

1. Laprol exhibits no pronounced effect on the kinetics of Cu(II) reduction at  $c_{lap}$  ranging up to 10 mg dm<sup>-3</sup>. Only a slight increase in overvoltage was observed in the region of low cathodic polarizations at  $c_{lap} = 100$  mg dm<sup>-3</sup>.

2. Strong inhibitive adsorption takes place in Sn|Sn(II) system. A simplified model involving the Temkin isotherm gives a satisfactory agreement between experimental and simulated current densities in the region of voltammogram plateau.

3. Characteristic minima develop on voltammograms obtained for the solutions containing Cu(II), Sn(II) and laprol. It seems probable that the adsorption layers resulting in strong inhibition might be formed of laprol and the products of Sn(II) reduction.

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**LAPROLO 2402 C ADSORBCIJOS ANT VARIO IR ALAVO ELEKTRODŲ VOLTAMPEROMETRINĖ CHARAKTERISTIKA**

S a n t r a u k a

Atliktas Cu(II) and Sn(II) redukcijos voltamperometri- nis tyrimas sulfatiniuose paviršiuje aktyvios medžiagos – laprolo 2402 C – tirpaluose. Sistemoje Cu|Cu(II) jokios žymesnės laprolo įtakos nenustatyta, kai jo koncentraci- ja ( $c_{\text{lap}}$ ) neviršijo 10 mg dm<sup>-3</sup>. Tirpaluose, kuriuose  $c_{\text{lap}} = 100$  mg dm<sup>-3</sup>, pastebėtas tik silpnas viršvoltažio padi- dėjimas mažų katodinių poliarizacijų srityje. Priešingai, sistemoje Sn|Sn(II) vyksta stipri inhibicinė adsorbci- ja. Supaprastintas modelis, kuriame panaudota Temkino izo- terma, duoda patenkinamą apskaičiuotų ir eksperimen- tinių srovės tankių sutapimą voltamperogramos plato srityje. Cu(II), Sn(II) ir laprolo tirpalų voltamperogramo- se atsiranda charakteringas minimumas. Adsorbciniai sluoksniai, sąlygojantys stiprią inhibiciją, gali būti suda- ryti iš laprolo ir Sn(II) redukcijos produktų.

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**ВОЛЬТАМПЕРОМЕТРИЧЕСКАЯ ХАРАКТЕРИСТИКА АДСОРБЦИИ ЛАПРОЛА 2402 С НА МЕДНОМ И ОЛОВЯННОМ ЭЛЕКТРОДАХ**

Р е з ю м е

Проведено вольтамперометрическое исследование вос- становления Cu(II) и Sn(II) в сульфатных растворах, содержащих лапрол 2402 С в качестве поверхностно- активного вещества. В системе Cu|Cu(II) не обнаружено