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Adsorption Behaviour of Laprol 2402 C on Copper Electrode

by A. Survila[*], Z. Mockus, S. Kanapeckaitė and M. Samulevičienė

Institute of Chemistry, Goštauto 9, LT 2600 Vilnius, Lithuania
E-mail: arvydass@ktl.mii.lt

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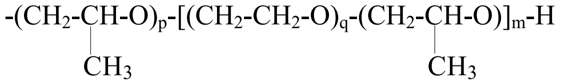
Voltammetry and EIS were applied to study the adsorption behaviour of laprol 2402 C (the copolymer of ethene and propene oxides) on a Cu electrode in strongly acidic Cu(II) sulphate solutions. Analysis of impedance data was carried out on the basis of adequate equivalent circuits, containing electric analogues of the electrochemical system. The results indicate that laprol displays a rather weak surface activity on copper in chloride-free solutions. Pronounced inhibition of Cu(II) reduction takes place, when micromolar amounts of chloride are added. A more compact surface layer involving Cl^- ions is thought to be formed under these conditions.

Key words: copper, polyether laprol, chloride, adsorption

Plating baths, used for producing bright copper coatings, usually contain polyether organic compounds in combination with some sulfur-containing additives. Polyethylene glycol (PEG), polypropylene glycol (PPG) are among the most widely used polyethers. Recently, laprol 2402 C with average molecular mass of *ca* 3200 was found to be an effective component for bright bronze plating [1,2]. An approximate formula of this compound may be written as X-O-X, where X represents the chain:



$$\text{-}(CH_2\text{-}\underset{\substack{|\\ CH_3}}{C}H\text{-}O)_p\text{-}[(CH_2\text{-}CH_2\text{-}O)_q\text{-}(CH_2\text{-}\underset{\substack{|\\ CH_3}}{C}H\text{-}O)]_m\text{-}H$$

with $p \approx 10$, $q \approx 12$, $m \approx 2$. As may be seen from above, this surface-active substance (SAS) might be treated as the block copolymer of PEG and PPG with expected similar adsorption behaviour.

A comprehensive overview, regarding the role of the two latter SAS in electrodeposition of bright copper coatings, has been provided by Stoychev [3,4]. It was concluded that the surface activity of polyethers depend on the electrode potential, the polyether molecular mass and concentration, as well as on the presence of other ions (particularly Cl^-) in the solution. The interaction between PEG (PPG) and Cu^+ (Cu^{2+}) ions, leading to the formation of respective complexes, was also discussed. It was stated that Cl^- ions might act as particles enhancing adsorption which, in turn, is re-

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[*] Author for correspondence. Tel.: +3702-612743; fax: +3702-617018.

sponsible for a strong inhibition of Cu(II) reduction. The possibility of gel formation, acting as a membrane between the bulk of the solution and the cathode surface, was also considered.

At the same time, some contradictions may be found in the literature. For instance, the 50–60 mV decrease in the open-circuit potential, caused by PEG addition, has been reported [5,6], this being indicative of the formation of moderately strong complexes. On the other hand, complexes between Cu^+ or Cu^{2+} and PEG are supposed to be unstable [3,4]. According to [7], PEG inhibiting effect is very strong even in chloride-free solutions and results in a decrease in current density of around three orders of magnitude. However, the same effect has also been found [5,8] to be much weaker.

Such different data seem to arise from poor purity of solutions. As has been emphasized [8], the effect of trace chloride is so large that any inhibition found on adding PEG to the base electrolyte, may well be the effect of chloride impurity. In this connection, we made an attempt to investigate the adsorption behaviour of laprol on copper electrode in solutions, sufficiently protected from trace Cl^-.

EXPERIMENTAL

The solutions under investigation contained 0.01 M $CuSO_4$ (Mallinckrodt, USA, with chloride impurities of 0.0005%) 0.6 M H_2SO_4, additives of $SnSO_4$ (analytical grade) and different amounts of laprol 2402 C, which was used as received. Deaeration of solutions was carried out by a pure argon stream passed through the solution before measurements for 0.5 h and over solutions when curves were recorded. Triply distilled water was used for solutions preparation. A Pt wire with 0.36 cm^2 surface area was used as working electrode substrate for impedance measurements. It was coated at 10 mA cm^{-2} by a 5–7 μm thick copper layer in a solution containing (g dm^{-3}): $CuSO_4 \cdot 5H_2O$ – 200, and H_2SO_4 – 50. A saturated Ag|AgCl, KCl electrode served as reference. To protect the solutions from Cl^- ions, a chloride-free electrolytic junction was used and changed after each experiment. Electrode potentials were converted to the standard hydrogen scale. Impedance measurements were carried out within a frequency (f) range from 10^{-1} to 5×10^4 Hz using a Zahner Elektrik (Germany) IM6 Impedance Spectrum Analyzer. Each experiment was repeated 3–4 times. Computer programs elaborated by Boukamp [9] were used for analyzing impedance spectra. In addition to these measurements, a conventional rotating disc technique was used with 5 mV s^{-1} potential scan rate. The working electrode (1 cm^2) was prepared in a similar way. All experiments were performed at 20°C.

RESULTS AND DISCUSSION

The surface activity of laprol can be reliably assessed from impedance data. For the most part, an effect of laprol is the same for both supporting electrolyte (0.6 M H_2SO_4) and that containing 0.01 M of Cu(II). A typical example, obtained under open-circuit conditions, is presented in Fig. 1. At $f > 100$ Hz, Nyquist plots actually coincide for laprol concentrations (c_{lap}) ranging up to 0.1 g dm^{-3}. The main effect of laprol is observed at low frequencies (< 5 Hz), when c_{lap} is comparatively high. Similar results were also obtained, when different cathodic polarizations were applied.

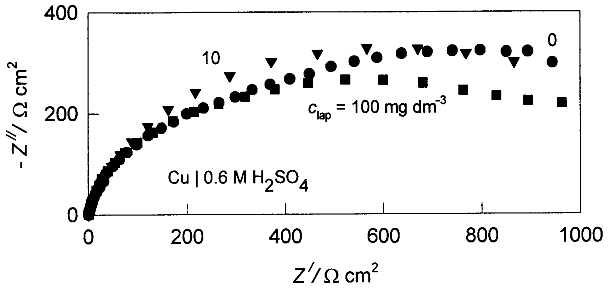

Figure 1. Nyquist plots obtained in supporting electrolyte under open-circuit conditions. Concentrations of laprol are indicated on the curves.

In contrast with the data obtained for PEG-containing Cu(II) solutions [5,6], no detectable influence of laprol on the open-circuit potential (E_{oc}) was found. On addition of this substance to 0.01 M Cu(II) solutions, E_{oc} varies within ± 2 mV and is in a good agreement with the equilibrium potential $E_{eq} = 0.245$ V, following from Nernst equation with an activity coefficient of Cu^{2+} 0.07 [10]. The highest laprol concentration used was 0.1 g dm^{-3} (the ratio of $c_{Cu(II)}/c_{lap}$ was close to that employed in the plating baths [1–4]). This quantity contains only *ca* 2 mM of oxygen atoms, capable to form copper complexes, that were reported to be weak [2,4]. Hence, the laprol concentration is too small to give rise for the detectable shift of E_{eq}.

Cathodic voltammograms obtained for solutions protected from traces of Cl^- ions exhibit some irregularities in the vicinity of –0.1 V, which are shaped like prewaves (Fig. 2). The reasons for such behaviour are not clear yet. However, there is no question, that the effect of laprol is weak. Voltammetric data obtained at $c_{lap} < 20$ mg dm^{-3} lie within experimental errors. Some effect of laprol is observed at a higher c_{lap} in the region of sufficiently low cathodic polarization. In contrast, the limiting current den-

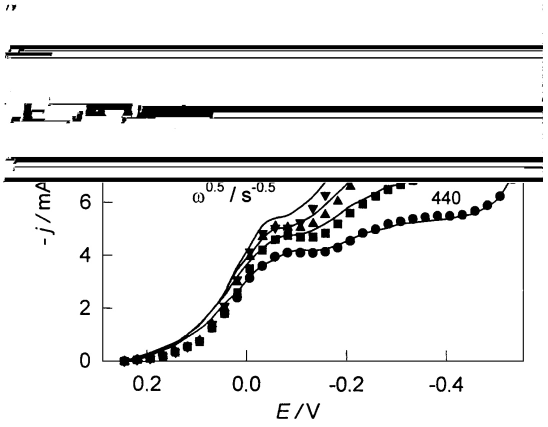

Figure 2. Voltammograms of Cu(II) reduction obtained for 0.01 M Cu(II) solutions at different rotating velocities of RDE indicated on the curves (rev per min). Data for laprol-free solutions and for those with $c_{lap} = 100$ mg dm^{-3} are displayed by lines and symbols respectively. Levich plot of current density, determined at –0.45 V, is given in the inset.

sity does not depend on c_{lap} and obeys the Levich equation with diffusion coefficient $D = 5.5\times10^{-6}$ cm^2 s^{-1} (see inset in Fig. 2).

Nyquist plots obtained in the presence of Cu(II) are quite reproducible and take the shape of arcs centered below the abscissa axis (Fig. 3). Some deviations from this shape may be found at the lowest frequencies. This effect becomes more pronounced at certain cathodic polarizations (Fig. 4), where linear parts of the plots resulting from diffusion processes are clearly visible. It is necessary to emphasize that a very stable direct current is set within *ca* 50 s and does not vary during the impedance measurements (see inset in Fig. 4). Quantitative analysis of impedance data requires some preliminary discussion. The electroreduction of Cu^{2+} is known to proceed by two consecutive one-electron transfers:

$$Cu^{2+} + e \qquad Cu^{+} \qquad (1) \qquad\qquad Cu^{+} + e \qquad Cu \qquad (2)$$

with exchange current densities j_{01} and j_{02} respectively. Such a mechanism may be described in terms of impedance invoking various methods. One of them consists of solving differential equations reflecting Fick's second law and accounting for the diffusive flow of the intermediate. For instance, such an approach has been used to obtain analytical expressions for the real (Z') and imaginary (Z''

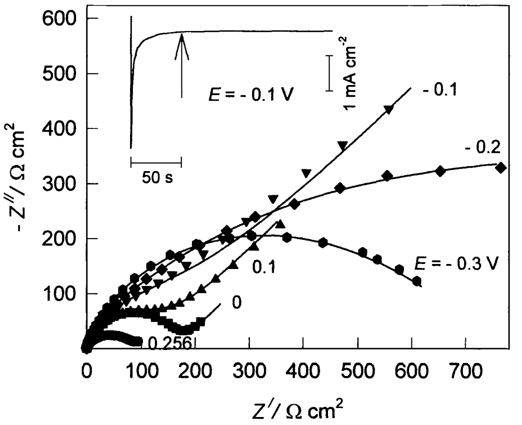

Figure 4. Nyquist plots obtained at different electrode potentials indicated on the curves. Comparison between experimental (symbols) and simulated (lines) data. Parameters of equivalent circuit are listed in Table 1. An example of current variation after switching on the indicated electrode potential is shown in the inset. The arrow shows the moment of start of the impedance recording.

elements in parallel are enclosed in parentheses). When charge transfer coefficients for both steps are equal to 0.5, then

$$j_{01} + j_{02} = \frac{RT}{F}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{3}$$

$$\frac{1}{j_{01}} + \frac{1}{j_{02}} = \frac{R_1 + R_2}{W_1 + W_2}\,\frac{1}{F\sqrt{D}}\left(\frac{1}{[\mathrm{Cu}^{2+}]} + \frac{4}{[\mathrm{Cu}^{+}]}\right) \tag{4}$$

In contrast with description code, here W_1 and W_2 are Warburg coefficients related to Warburg impedance (Z_W) by

$$Z_{Wk} = \frac{W_k(1-i)}{\sqrt{\omega}} \tag{5}$$

where $\omega = 2\pi f$, $k = 1, 2$ and $i = \sqrt{-1}$. The Warburg admittance (Y_W) may be given by

$$Y_W = (Z_W)^{-1} = Y_0(i\omega)^{0.5} \tag{6}$$

Equations (3) and (4) are valid in the case of one-dimensional semi-infinite diffusion under equilibrium (open-circuit) conditions. The total electrode impedance is obtained, when such extra parameters as the ohmic resistance of solution (R_Ω) and capacitance of the double electric layer (C_{dl}) are added. The circuit $R_\Omega([R_1W_1][R_2W_2]C_{dl})$ is applicable for a somewhat idealized system and does not account for the effects arising from the roughness of the electrode nor the limited space of diffusion. A characteristic feature of the problem under discussion lies in the fact that the faradic elements are functions of kinetic and diffusion parameters of both steps (1) and (2). This is not the case of one-step charge transfer, which may be separated from diffusion processes. Analysis has shown that the experimental data can be described with a rather high accuracy, using a slightly modified equivalent circuit, where C_{dl} is replaced by a constant phase element (CPE) Q_{dl} with admittance equal to $Y_0(i\omega)^n$ [13]. At $n = 1$, this element transforms into capacitance. Established parameters are listed in Table 1; the comparison of experimental and simulated data for this circuit is shown in Figs 4 and 5. Both the real and imaginary components of impedance, as well as the phase angle (ϕ) coincide quite well with respective characteristics of the equivalent circuit. It may be also seen that ϕ is reproduced better than the impedance (*cf* Figs 3 and 5). Since the former is known to be independent of surface area, insignificant Z discrepancies observed at repeated measurements (Fig. 3) are attributable to the respective changes in real surface area in the course of experiments. Considering that the factor n characterizing Q_{dl} is close to 1 (Table 1), this CPE may be treated as a non-ideal double layer capacitance. A very similar value of Y_0 (1.35×10^{-4} S cm^{-2} s$^{0.8}$) was also obtained for laprol-free solutions at E_{oc} [17]. The $[(R_1C_1)(R_2C_2)]$ equivalent circuit has been proposed for modeling of PEG adsorption in 0.24 M $CuSO_4$ solutions [5]. The elements R_2 and C_2 have been associated with some process controlled by interfacial or film diffusion. However, we have not identified any additional elements indicative of the adsorption-controlled steps. Although the equivalent circuit used was found to fit the experimental data reasonably well, we failed to obtain plausible kinetic parameters even under open-circuit conditions. Deviations from ideality of the electrode surface, some uncertainty in $[Cu^+]$ (see Eqn. (4)) may be mentioned among the reasons for such a result. This problem becomes more complicated for cathodic polarizations and needs additional information on surface concentrations of Cu^{2+} and Cu^+, partial current densities, *etc*. In spite of this, it is possible to conclude, that laprol exhibits low surface activity on copper in Cl^--free solutions. The situation changes radically, when quite low amount of chlorides is added. The effect of chlorides becomes detectable even at $c_{Cl^-} > 0.1$ mM and does not depend on the nature of cation (Na^+ or K^+). Besides, this effect is opposite for laprol-free and laprol-containing solutions. In the former case, an addition of chlorides results in the depolarization of the cathodic process (Fig. 6a). In contrast, a significant increase in cathodic polarization with c_{Cl^-} takes place in the presence of laprol (Fig. 6b). This phenomenon is in agreement with impedance data (Fig. 7): an addition of chlorides results in the increase of total impedance. It follows from the data given in the three first lines of Table 1 that the double layer capacitance decreases with c_{Cl^-}.

Table 1. Parameters of equivalent circuit $R_\Omega(Q_{dl}[R_1W_1][R_2W_2])$ obtained for 0.01 M Cu(II) solution containing 10 mg dm^{-3} of laprol at different electrode potentials *E*. $R_\Omega = 0.47$ Ω cm^2.

E	Q_{dl}		R_1	W_1	R_2	W_2	Freq. error
V	10^6 Y_0, S cm^{-2} s^n	n	Ω cm^2	10^4 Y_0, S cm^{-2} s$^{0.5}$	Ω cm^2	10^4 Y_0, S cm^{-2} s$^{0.5}$	%
0.256	148	0.830	~3	9.08	88.9	890	1.5
0.256[a)]	97.4	0.808	25.6	7.45	499	54.0	2
0.254[b)]	43.1	0.877	22.6	6.34	1050	13.4	2
0.100	110	0.882	440	1.13	172	201	2
0.000	100	0.913	176	1.94	153	37.7	1.5
–0.100	94.7	0.928	98	4.78	309	14.6	2–4
–0.200	100	0.917	89	7.30	1350	92.4	2
–0.300	98.2	0.920	28	3.77	733	1010	2
–0.400	101	0.914	$\rightarrow 0$	1.47	232	–	2.5

[a)] $c_{Cl^-} = 3$ μM, [b)] $c_{Cl^-} = 150$ μM.

The results obtained may be interpreted in terms of chemical interaction between laprol, chloride and intermediate Cu^+. The possibility of formation of similar complexes containing PEG has been reported earlier [3,4]. It was supposed that the ratio of oxygen and Cu^+ equals 4, but no stability constants have been determined. An esti-

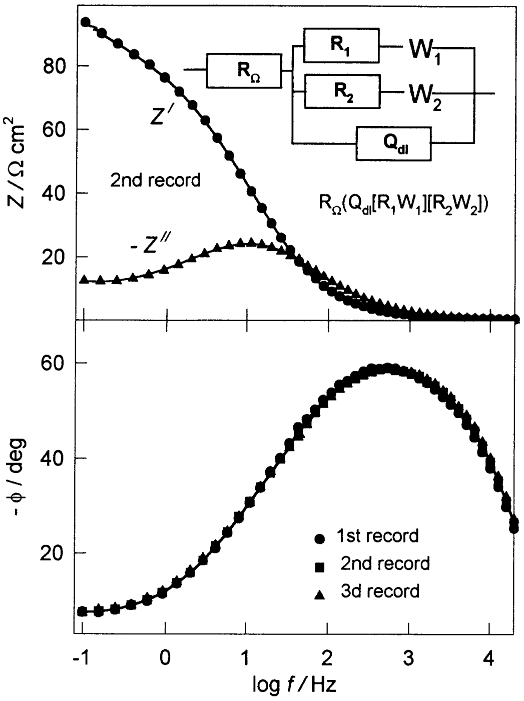

Figure 5. Comparison between experimental (symbols) and simulated (lines) impedance spectra (upper part) and phase shift (lower part). The equivalent circuit and its description code are also presented.

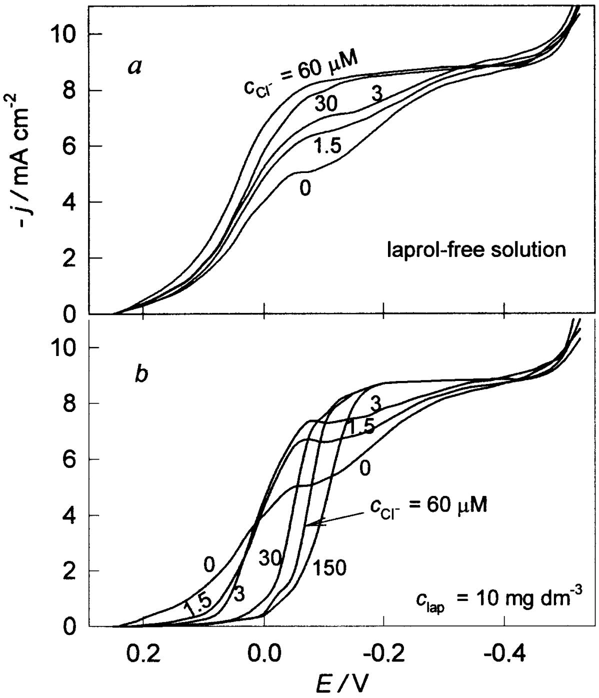

Figure 6. Effect of chloride on voltammograms obtained for laprol-free (part *a*) and laprol-containing (part *b*) solutions at 1230 rev. per min. Chloride concentrations are indicated at the curves.

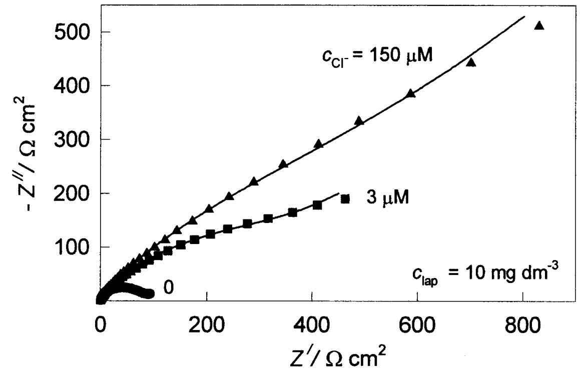

Figure 7. Effect of chloride on Nyquist plots obtained for the solution containing 10 mg dm^{-3} of laprol. Comparison between experimental (symbols) and simulated (lines) data. Parameters of equivalent circuit are listed in Table 1. Chloride concentrations are indicated on the curves.

mation of Cu$^+$ equilibrium concentration in the system under investigation performed using material balance equations (for details see [18]) yields 77 μM. Hence, a sufficient excess of laprol with respect to Cu$^+$ exists in the system and the formation of complexes mentioned above seems to be quite probable. In general, the results obtained testify that chloride ions enhance the adsorption of laprol on copper electrode.

They are known as species capable for a specific adsorption and acting as bridging particles in co-adsorption with other SAS. Similar but much stronger effects were also observed on addition of milimolar amounts of other halides. These phenomena are of special interest and are planned for publication in the nearest future.

CONCLUSIONS

Voltammetric data indicate that the effect of laprol on Cu(II) reduction in strongly acidic sulphate solutions is negligible, when the concentration of this substance (c_{lap}) does not exceed 20 mg dm^{-3}. A slight decrease in current density is observed only at higher c_{lap} in the region of sufficiently low cathodic polarization. The weak surface activity of laprol also follows from impedance data. An analysis of impedance spectra carried out on the basis of adequate equivalent circuits shows that the double layer capacitance is actually independent of both c_{lap} and electrode potential. No elements indicative for adsorption-controlled steps were identified. An addition of milimolar amounts of chloride enhances the laprol adsorption, giving rise to a decrease in double layer capacitance and to a significant increase in cathodic polarization of Cu(II) reduction. It is suggested that the formation of complexes involving Cu$^+$, Cl$^-$ and laprol is responsible for such an effect.

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