
Halide-enhanced adsorption of polyether laprol 2402 C on copper electrode

Arvydas Survila,
Zenius Mockus,
Stasė Kanapeckaitė and
Meilutė Samulevičienė

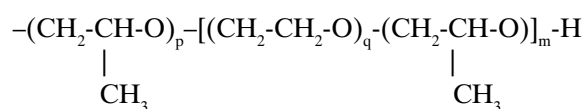
*Institute of Chemistry,
A. Goštauto 9,
LT 2600 Vilnius, Lithuania*

EIS technique was applied to study the adsorption behaviour of the polyether laprol 2402 C on Cu electrode in strongly acidic solutions. The impedance spectra obtained for halide- and/or laprol-containing Cu(II) solutions may be well described using the equivalent circuit $R_{\Omega}([R_1Q_1][R_2Q_2]Q_{dl})$ allowing to separate the faradaic elements R_1, Q_1, R_2, Q_2 from the constant phase element Q_{dl} reflecting double-layer capacitance. Halides act as surface-active anions increasing double-layer capacitance in laprol-free solutions. Adsorption of the polyether laprol 2402 C is enhanced by the halides in the sequence $Cl^- < Br^- < I^-$. An additional [RL] sub-circuit was found to occur in the case of iodide-containing solutions, this being indicative of the processes controlled by potential-dependent adsorption.

Key words: copper, polyether laprol, halides, adsorption, enhancement

INTRODUCTION

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



with $p \approx 10$, $q \approx 12$, $m \approx 2$. As one can see from the above, this SAS might be treated as a block copolymer of PEG and PPG with expected similar adsorption behaviour.

According to the comprehensive reviews provided by Stoychev et al. [3, 4], the adsorption of polyethers on copper substrate can be weak or strong, depending on the cathodic polarization, solution composition and, especially, on the presence of other ions (particularly Cl^-) in the solution. It has been stated that Cl^- ions can act as particles enhancing SAS adsorption which, in turn, is responsible for a strong inhibition of Cu(II) reduction.

At the same time, some contradictions can be found in the literature. For instance, a 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], the inhibiting effect of PEG is very strong even in chloride-free solutions and results in a decrease in current density by around three orders of magnitude. However, the same effect has also been found [5, 8] to be much weaker. As have been suggested in [9], Cl^- ions suppress a specific adsorption of PEG molecules occurring in H_2SO_4 solutions, and all models assuming the adsorption of neutral PEG molecules cannot be correct. Nevertheless, the authors of Ref. [9] came to the conclusion that it is impossible to predict a correct mechanism for copper electrodeposition in the presence of PEG and chloride.

Some different literature data seem to arise from a poor control of the purity of solutions. As has been emphasized [8], the effect of trace chloride is so great that any inhibition found on adding PEG to the base electrolyte may well be the effect of chloride impurity. Certainly, voltammetric and impedance data [10–12] obtained recently for solutions protected from chloride traces have shown a rather weak surface activity of laprol on copper electrode.

It is well known that chloride improves the anodic process, and therefore this substance is a necessary

component of most plating baths. It seems plausible that chloride, as well as the rest halides, may affect the adsorption of laprol on copper. A comparison of the data obtained for different halides might provide a useful insight into the nature of copper electrodeposition.

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 (analytical grade) as a supporting electrolyte, potassium halides (high purity) and laprol 2402 C (Russia) which was used as received. Thrice-distilled water was used for the preparation of solutions. A pure argon stream was passed through the solutions before measurements for 0.5 h and over solutions when the curves were recorded.

A Pt wire with a surface area of 0.36 cm^2 was used as a substrate for preparation of working electrodes. It was coated at 10 mA cm^{-2} with a $5\text{--}7 \text{ }\mu\text{m}$ thick copper layer in a solution containing (g dm^{-3}): $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} - 200$, $\text{H}_2\text{SO}_4 - 50$. The working electrodes were rinsed with water, immediately immersed into the solution under investigation and kept in it for at least 5 minutes before measurements. An $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$ electrode served as a reference. To protect the solutions from Cl^- traces, a chloride-free electrolytic junction was used and changed after each experiment. The electrode potentials were converted to the standard hydrogen scale.

Impedance measurements were carried out with 5 mV AC-voltage amplitude within the frequency (f) range from 10^{-1} to 5×10^4 Hz using a Zahner Elektrik (Germany) IM6 Impedance Spectrum Analyzer. Each record took about 5 minutes and was repeated 3–4 times. An average reproducibility of impedance was at 95% confidence level at $f > 1$ Hz. Only in the case of iodide-containing solutions a tendency to some increase in the impedance with exposure time was observed. Nevertheless, the reproducibility of the phase shift (ϕ) was nice in all the cases. Computer programs elaborated by Boukamp [13] were used to analyze the impedance spectra.

RESULTS AND DISCUSSION

It is common knowledge that $\text{Cu}(\text{II})$ electroreduction proceeds by two consecutive one-electron transfers: $\text{Cu}^{2+} + e \rightarrow \text{Cu}^+$ and $\text{Cu}^+ + e \rightarrow \text{Cu}$. Halides are known to form coordination bonds with most of d -metal ions including both Cu^{2+} and Cu^+ [14]. Micromolar concentrations of halides are not suffi-

cient to change essentially the state of Cu^{2+} aqua-complexes in the bulk of 0.01 M $\text{Cu}(\text{II})$ solution. However, the possibility of interaction between intermediate Cu^+ ions and halides should be taken into account, since an estimation of equilibrium Cu^+ concentration generated by the $\text{Cu} + \text{Cu}^{2+} \rightarrow 2\text{Cu}^+$ reaction yields only $77 \text{ }\mu\text{M}$ [12]. Though Cu^+ complexes with some polyethers have been reported to be weak [3, 4], the possibility of their formation cannot be neglected, either. The interactions under discussion seem to be of considerable importance when the net cathodic process involves adsorption steps.

Experimental data obtained for laprol-free solutions (Fig. 1) are indicative of a significant effect of halides on impedance spectra. The total impedance involving real (Z' , positive values) and imaginary (Z'' , negative values) components increases in the sequence: $\text{Cl}^- < \text{Br}^- < \text{I}^-$. An addition of chloride gives rise to a decrease of impedance as compared with that obtained for halide-free solution (dashed lines in Fig. 1). This result is in accordance with voltammetric data [12]: addition of chloride results in a decrease of cathodic overvoltage. The rest halides (Br^- and I^-) exert an opposite influence on impedance spectra.

As mentioned above, laprol exhibits a weak surface activity on copper electrodes in halide-free solutions. No pronounced effect on voltammetric [11, 12] and impedance [10, 12] characteristics has been detected at laprol concentrations (c_{lap}) ranging up to 10 mg dm^{-3} . Only a slight increase in overvoltage has been observed in the region of low cathodic polarization at $c_{\text{lap}} = 100 \text{ mg dm}^{-3}$. According to

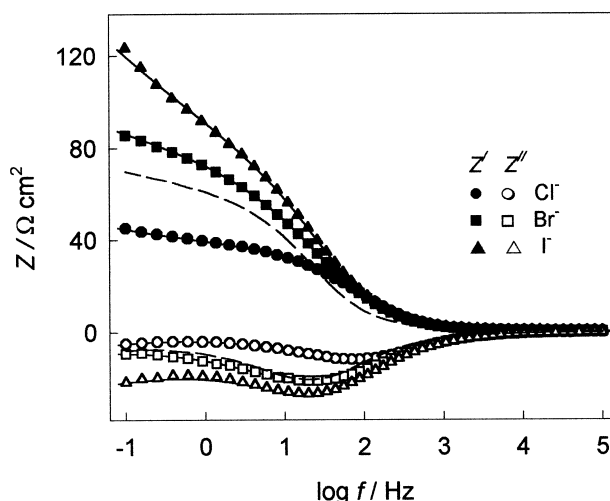


Fig. 1. Impedance spectra obtained for laprol-free 0.01 M $\text{Cu}(\text{II})$ solutions containing none (dashed lines) and $30 \text{ }\mu\text{M}$ of different halides. Comparison of experimental (symbols) and simulated (solid lines) data. Parameters of equivalent circuit are listed in Table. Open-circuit conditions, $E_{\text{oc}} = 0.253 \pm 0.002 \text{ V}$

[12], the effect of chloride is opposite for laprol-free and laprol-containing solutions. In the former case, addition of chloride results in depolarization of the cathodic process. In contrast, a significant increase in cathodic polarization with c_{Cl^-} was observed in the presence of laprol. The latter effect was found to become stronger in the sequence mentioned above [15].

Voltammetric as well as impedance characteristics are very sensitive to the presence of halides. The effect of chloride becomes detectable even at $c_{\text{Cl}^-} > 0.1 \mu\text{M}$; this limit is at least one order of magnitude lower for Br^- and I^- . Addition of halides into laprol-containing solutions results in a significant increase in total impedance (Fig. 2), which is most pronounced at sufficiently low frequencies, *i.e.* in the region where kinetic characteristics of faradaic processes dominate over adsorption features. To separate these phenomena, an analysis of impedance data was carried out on the basis of adequate equivalent circuits containing electric analogues of the electrochemical system. The equivalent circuit modelling the consecutive charge transfer process has been proposed in [16]. It contains two parallel sub-circuits, each including charge transfer resistance (R) and Warburg impedance (W). This construction should be shunted by double-layer capacitance (C_{dl}) with the following addition of the ohmic resistance of the solution (R_{Ω}). According to [13], the description code of this circuit may be written as $R_{\Omega}([R_1W_1][R_2W_2]C_{\text{dl}})$ (here elements in series are given in square brackets and elements in parallel are in parentheses). Such circuit is valid for ideally smooth electrode surfaces in the absence of other processes, including adsorption-controlled charge transfer.

In the case of non-ideal real systems, a modified equivalent circuit is often used, where W and C_{dl} are replaced by constant phase elements (CPE) Q with admittance equal to $Y_0(j\omega)^n$, where $\omega = 2\pi f$ and $j = \sqrt{-1}$. At $n = -1, 0, 0.5$ and 1 , CPE transforms into inductance, resistance, Warburg impedance and capacitance respectively [17]. Analysis has shown that the experimental data can be described with a 2% frequency error using the equivalent circuit $R_{\Omega}([R_1Q_1][R_2Q_2]Q_{\text{dl}})$. The established parameters are listed in Table; a comparison of experimental and simulated data for this circuit is shown in Figs. 1 and 2.

Considering that the factor n characterizing Q_{dl} is close to 1, this CPE may be treated as a non-ideal double-layer capacitance. Elements R_1 and R_2

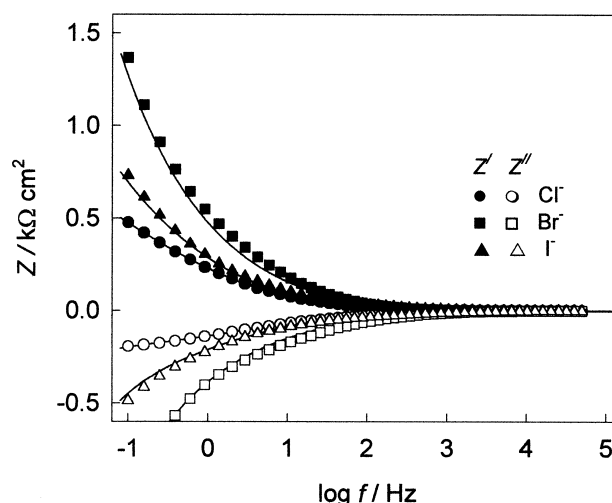


Fig. 2. The same as in Fig. 1 on addition of 10 mg dm^{-3} of laprol. E_{oc} is equal to 0.255, 0.232 and 0.260 V for chloride-, bromide- and iodide-containing solutions respectively

are attributable to the respective charge transfer resistances. CPEs Q_1 and Q_2 determined for laprol-containing solutions might be treated as Warburg impedances to some extent (n is close to 0.5), but this is not the case of laprol-free solutions, especially when the CPE Q_1 is concerned (Table). This circumstance suggests that some additional sub-circuits have not been identified. In the case of laprol-free solutions, Q_{dl} increases in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$. This effect is well known for different electrodes, including Hg, and is indicative of respective increase in specific adsorption of listed halides. In contrast, the effect of halides is inverted when laprol is present. At the same time, resistances R_1 and R_2 increase to a great extent. These phenomena show that halides enhance laprol adsorption which in its turn reduces the rate of charge transfer process.

Table. Parameters of equivalent circuit $R_{\Omega}([R_1Q_1][R_2Q_2]Q_{\text{dl}})$ obtained for 0.01 M Cu(II) solutions containing 30 μM of different halides. $R_{\Omega} = 0.48 \Omega \text{ cm}^2$. Dimensions: $[R] = \Omega \text{ cm}^2$, $[Y_0] = \text{S cm}^{-2} \text{ s}^n$.

Halide	R_1	Q_1		R_2	Q_2		Q_{dl}	
		$10^2 Y_0$	n		$10^4 Y_0$	n	$10^6 Y_0$	n
a) laprol-free solutions								
Cl ⁻	39	15.7	0.379	0.4	7.7	0.523	29	0.973
Br ⁻	75	6.7	0.224	1.2	9.3	0.499	39	0.950
I ⁻	35	1.2	0.142	17	2.3	0.627	62	0.902
b) $c_{\text{lap}} = 10 \text{ mg dm}^{-3}$								
Cl ⁻	700	0.67	0.424	6.3	10.6	0.469	41.7	0.892
Br ⁻	1900	0.04	0.446	26	5.2	0.493	14.6	0.950
I ⁻	920	0.17	0.474	8.3	7.7	0.531	10.6	0.955

It should be emphasized that impedance characteristics strongly depend on the electrode potential (E). In turn, variations of Z with E depend both on c_{lap} and c_{hal} . An example of experimental data shown in Fig. 3 is typical of all the halides at $c_{\text{hal}} = 30 \mu\text{M}$. Even a small E shift from its open-circuit value (E_{oc}) results in a significant increase in Z (cf curve a in Fig. 3 and the curve for bromide in Fig. 2). Further, Z decreases, passes the minimum and increases again. A comparison of the data obtained at the same E for bromide- and iodide-containing solutions shows that the impedance for the latter solutions is 2–3 times higher than that in the presence of bromide. Consequently, the inhibitive effect of halides according to the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$ is clearly evident for cathodically polarized electrodes. Some inversion in this sequence obtained under open-circuit conditions (Fig. 2) seems to result from the fact that E_{oc} depends on the halide nature and is most negative in the presence of bromide in laprol-containing solutions (see the caption of Fig. 2).

The impedance obtained at different cathodic polarizations may be well described using the same equivalent circuit as at the open-circuit potential. Consequently, no substantial changes in the mechanism are probable. Since iodide ions show the highest surface activity, specification of the reasonable equivalent circuit is possible in this case. Insertion of the additional [RL] sub-circuit makes it possible to describe the experimental data with excellent (0.5% frequency error) precision (Fig. 4). The presence of the above sub-circuit is typical of the processes controlled by potential-dependent adsorption (see, e.g., [18]).

Co-adsorption of laprol and halides seems to be of irreversible nature. It is particularly remarkable

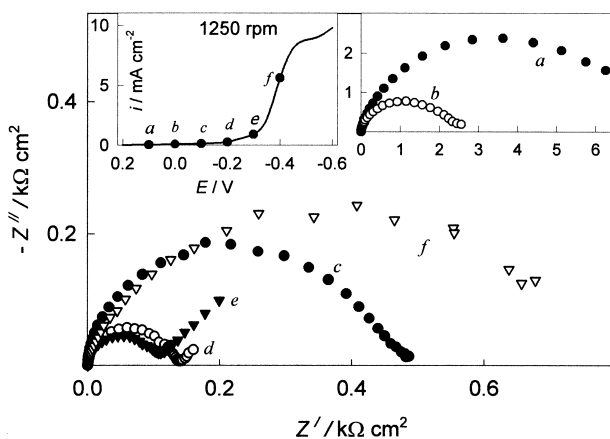


Fig. 3. Nyquist plots obtained for 0.01 M Cu(II) solutions containing $30 \mu\text{M}$ of bromide and 10 mg dm^{-3} of laprol. The left inset shows the position of the electrode potentials applied.

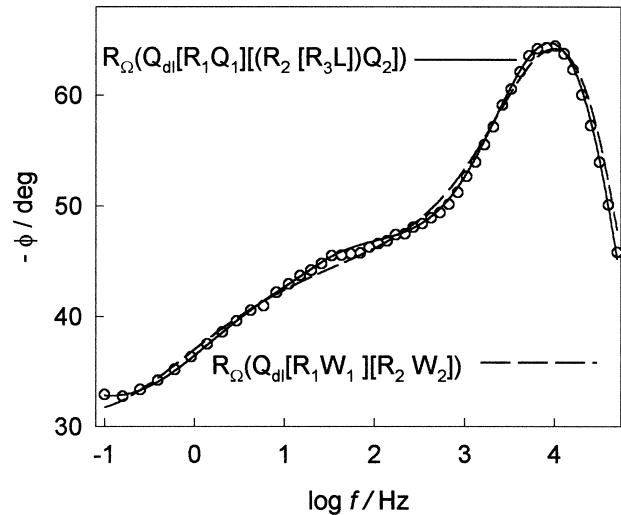


Fig. 4. Phase shift spectrum obtained at E_{oc} for Cu|Cu(II) system containing laprol and iodide. Comparison between experimental (symbols) and simulated (lines) data obtained for indicated equivalent circuits. The case with [RL] sub-circuit ($R = 2.1 \text{ k}\Omega\text{cm}^2$, $L = 15 \text{ H cm}^2$) is preferable

that the effect of halides actually disappears when a $-0.3 - -0.5 \text{ V}$ electrode potential is applied for 10–15 minutes before measurements under open-circuit conditions (Fig. 5). This takes place only at sufficiently low halide concentrations not exceeding $ca 5 \mu\text{M}$. The data obtained show that a certain amount of halides is utilized during copper electrodeposition and can be incorporated into the coating. Preliminary X-ray photoelectron spectroscopy data have shown that about 10 atomic % of bound halide may be found on the electrode surface

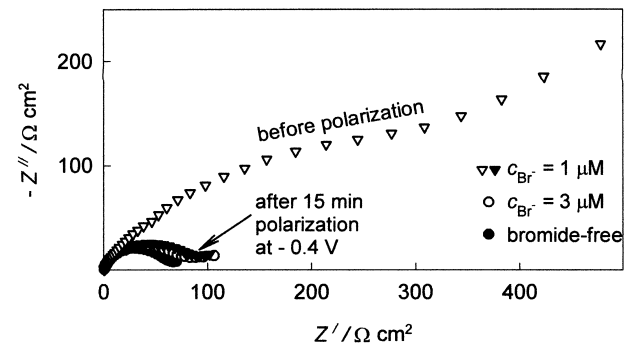


Fig. 5. Nyquist plots obtained under open-circuit conditions for 0.01 M Cu(II) solutions containing 10 mg dm^{-3} of laprol and different amounts of Br. The effect of bromide actually disappears after preliminary cathodic polarization

CONCLUSIONS

1. Impedance spectra obtained for halide- and/or laprol-containing Cu(II) solutions may be well-described using the equivalent circuit $R_{\Omega}([R_1Q_1]([R_2Q_2]Q_{dl}))$

making it possible to separate the faradaic elements R_1 , Q_1 , R_2 , Q_2 from the constant phase element Q_{dl} reflecting double-layer capacitance.

2. Halides Cl^- , Br^- and I^- act as surface-active anions increasing double-layer capacitance in laprol-free solutions. The adsorption of polyether laprol 2402 C is enhanced by halides in the sequence: $Cl^- < Br^- < I^-$.

3. An additional [RL] sub-circuit, typical of processes controlled by potential-dependent adsorption, was found to occur in the case of iodide-containing solutions.

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**A. Survila, Z. Mockus, S. Kanapeckaitė,
M. Samulevičienė**

HALOGENIDŲ SUSTIPRINTA POLIETERIO LAPROLO 2402 C ADSORBCIJA ANT VARIO ELEKTRODO

S a n t r a u k a

Taikant elektrocheminio impedanso spektroskopijos (EIS) metodą, ištirta polieterio laprolo 2402 C adsorbcinė elgsena ant vario elektrodo labai rūgščiuose tirpaluose. Impedanso spektrus, gautus Cu(II) tirpaluose su halogenidais ir/arba laprolu, gerai aprašo ekvivalentinė grandinė $R_1([R_1Q_1][R_2Q_2]Q_{dl})$, įgalinanti atskirti faradėjinius elementus R_1 , Q_1 , R_2 , Q_2 nuo pastoviosios fazės elemento Q_{dl} , atspindinčio dvigubojo sluoksnio talpą. Halogenidai Cl^- , Br^- ir I^- veikia kaip paviršiuje aktyvūs anijonai, didindami dvigubojo sluoksnio talpą tirpaluose be laprolo. Jie stiprina polieterio laprolo 2402 C adsorbciją sekoje: $Cl^- < Br^- < I^-$. Tirpalų su jodidu atveju aptikta papildoma [RL] sub-grandinė, būdinga procesams, kuriuos kontroliuoja nuo potencialo priklausanti adsorbcija.