
Halide-suppressed adsorption of polyether laprol 2402 C on tin electrode

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Voltammetry and EIS technique were applied to study the adsorption behaviour of the polyether laprol 2402 C on Sn electrode in strongly acidic solutions. The impedance spectra obtained for halide- and/or laprol-containing Sn(II) solutions may be well described using the equivalent circuit $R_{\Omega}([R_1Q_1]Q_{dl})$ involving ohmic resistance R_{Ω} , charge transfer resistance R_1 and constant phase elements Q_1 , Q_{dl} reflecting Warburg impedance and double-layer capacitance respectively. Halides exert no influence on impedance spectra in laprol-free solutions. In contrast, the inhibitive adsorption of laprol was found to be partially suppressed by the halides in the sequence $Cl^- < Br^- < I^-$ due to competition between the adsorbates. Negative impedance was detected in the region of the negative slope of voltammograms where the double-layer capacitance acquires the lowest value. However, this value is higher than in halide-free solutions.

Key words: tin, polyether laprol, halides, adsorption, impedance

INTRODUCTION

Codeposition of metals can be often controlled by ligands and surface-active substances (SAS). Polyether laprol 2402 C (a product of polycondensation of ethene and propene oxides) with average molecular mass of *ca* 3200 has been recently applied as an effective component for bright bronze plating [1, 2]. Voltammetric and impedance investigations have shown [3–6] that this SAS exhibits different behaviour on copper and tin electrodes. The surface activity of similar polyethers, such as polyethylene glycol (PEG), on copper substrate is considerably enhanced by chloride (see [7–9] and references therein), whereas their adsorption in solutions reliably protected from chloride traces is quite weak [3–5]. Although the data concerning copper electrodes are rather comprehensive, a prediction of correct mechanism for copper electrodeposition in the presence of polyethers remains problematic [9].

As mentioned above, adsorption of the SAS under discussion strongly depends on the nature of substrate. Similar to copper, the surface activity of PEG on platinum is also very low [10], this being not the case of tin electrode [6, 11]. Significantly less data concerning the latter object are available in the literature. The onset and development of characteristic voltammetric minimum has been observed on addition of laprol to bronze plating solu-

tions [1, 2, 4, 6]; some effects of inhibitive adsorption of the SAS on tin or its alloys have been also reported [12–15].

It is common knowledge 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 tin. A comparison of the data obtained for different halides might provide a useful insight into the nature of tin electrodeposition.

EXPERIMENTAL

The solutions under investigation contained 0.01 M SnSO_4 , 1 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 with a copper sublayer and then by a 5–7 μm tin layer at 10 mA cm^{-2} in a solution containing (g dm^{-3}): SnSO_4 – 50, H_2SO_4 – 160, laprol 2402 C – 1. 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 Ag|AgCl|KCl(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 × 10⁴ Hz using a Zahner Elektrik (Germany) IM6 Impedance Spectrum Analyzer. Each record took about 5 minutes and was repeated 3–4 times. Computer programs elaborated by Boukamp [16] were used to analyze the impedance spectra.

Voltammetric data were obtained using a conventional rotating disc technique with a 5 mV s⁻¹ potential scan rate. Electrodes with 1 cm² surface area were prepared in a similar way.

All experiments were performed at 20 °C.

RESULTS AND DISCUSSION

The main regularities of laprol adsorption on tin electrodes have been reported earlier [11]. It has been established that this SAS does not affect the open-circuit potential (E_{oc}) but gives rise to a significant decrease in cathodic current density (i) throughout the entire region of cathodic polarizations. A similar behaviour of laprol was also observed for halide-containing solutions. A typical example illustrating experimental data obtained for all the halides under investigation is given in Fig. 1.

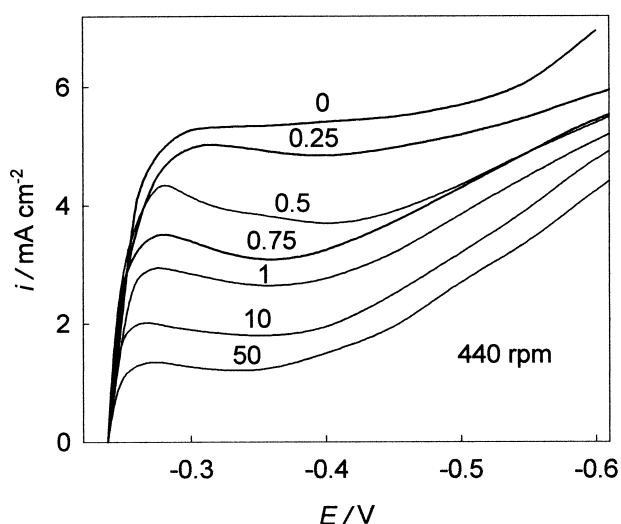


Fig. 1. Effect of laprol on voltammograms recorded in 0.01 M Sn(II) solutions containing 30 μM of bromide. Concentrations of laprol (mg dm⁻³) are indicated at the curves. Rotating disc electrode technique at 440 revolutions per minute

Even very low concentrations of laprol (c_{lap}) exhibit the ability to impede the reduction of Sn(II) approaching the limit at $c_{lap} = 100$ mg dm⁻³. According to the data obtained, the limiting current density follows Levich behaviour in laprol-free solutions. The effect of intensity of forced convection reduces progressively with c_{lap} and becomes negligible at $c_{lap} > 10$ mg dm⁻³. However, the above effects are less pronounced in halide-containing solutions as compared to those observed in the absence of halides [11]. Data in Fig. 2 show the

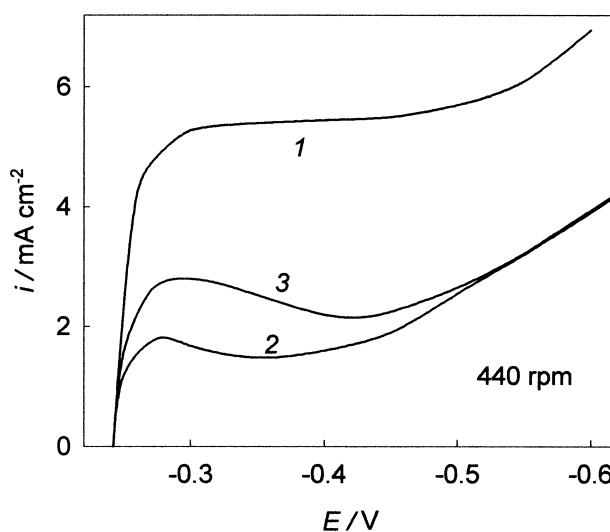


Fig. 2. Voltammograms obtained at 440 rev min⁻¹ for: 0.01 M Sn(II) solution (curve 1), solution containing 10 mg dm⁻³ of laprol (curve 2), the latter on addition of 30 μM of iodide (curve 3)

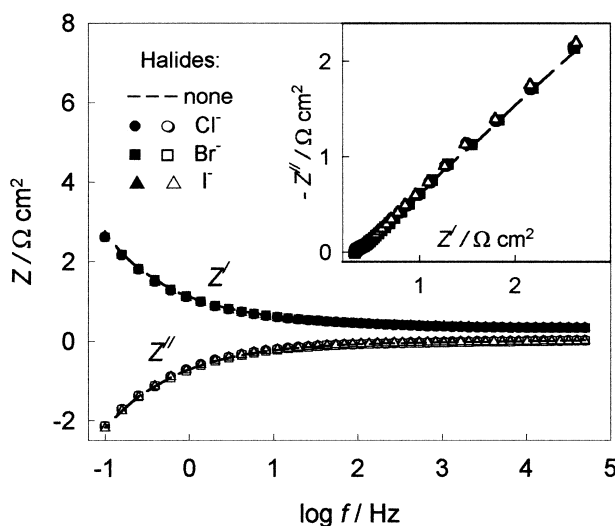


Fig. 3. Impedance spectra obtained for laprol-free 0.01 M Sn(II) solutions containing none (dashed lines) and 30 μM of different halides (symbols). Respective Nyquist plots are shown in the inset. Open-circuit conditions at $E_{oc} = -0.240 \pm 0.001$ V

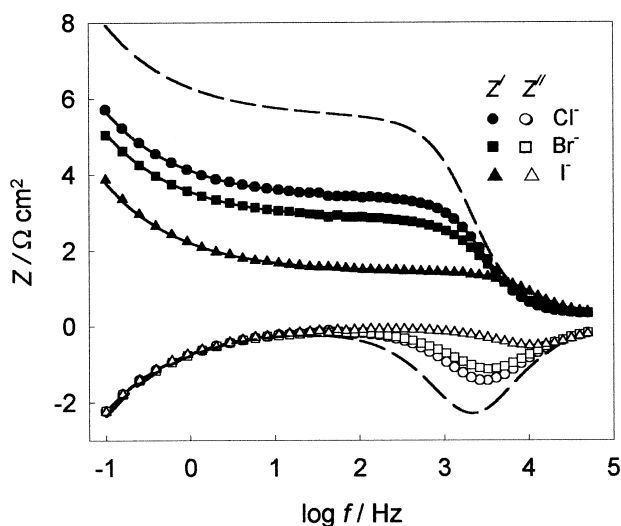


Fig. 4. Impedance spectra obtained at open-circuit conditions for 0.01 M Sn(II) solutions containing 10 mg dm⁻³ of laprol, none (dashed lines) and 30 μM of different halides (symbols). Comparison of experimental (symbols) and simulated (solid lines) data. Parameters of equivalent circuit are listed in Table (part a)

influence of iodide, which is the most effective halide responsible for the suppression of inhibitive adsorption of laprol. The rest halides show a lower activity and form the following sequel: Cl⁻<Br⁻<I⁻.

It is particularly remarkable that no similar effects were observed for laprol-free solutions. Both voltammetric and impedance (Fig. 3) characteristics, involving real (Z' , positive values) and imaginary (Z'' , negative values) components, remain actually the same and do not depend on the presence or on the nature of halides. The unit slope of Nyquist plots (inset in Fig. 3) is indicative of the electrochemical process controlled mainly by diffusion. In this case, only the estimation of the exchange current density ($i_0 \approx 0.1$ A cm⁻²) is available from experimental data. Moreover, nothing can be concluded on the surface activity of the halides.

In accordance with voltammetric data, the situation changes radically in laprol-containing solutions. Addition of halides results in a decrease of the total impedance (Fig. 4), this effect being stronger in the sequence presented above.

An appropriate equivalent circuit containing electric analogues of the electrochemical system can be proposed. The faradaic process may be represented by charge transfer resistance R_1 and Warburg impedance W_1

in series. In the case of non-ideal systems, the latter element is often replaced by the constant phase element (CPE) Q_1 with the admittance equal to $Y_0(j\omega)^n$, where $\omega = 2\pi f$ and $j = \sqrt{-1}$. At $n = 0.5$, Q_1 transforms into W_1 [17]. This sub-circuit should be shunted by the double layer capacitance C_{dl} (or by CPE Q_{dl} at n close to 1 [17]) with following addition of the ohmic resistance of the solution (R_Ω). According to [16], the description code of this circuit may be written as $R_\Omega([R_1Q_1]Q_{dl})$ (here elements in series are given in square brackets and elements in parallel are in parentheses). Experimental data can be described with a 2% frequency error using this equivalent circuit (Fig. 4). The established parameters are listed in Table, part a. It should be noted that the circuit given in Table 1 transforms into that under discussion at $R_2 \rightarrow \infty$.

Considering that the factor n characterizing Q_1 in open-circuit conditions is close to 0.5, this CPE may be treated as Warburg impedance. Actually, its conductivity determined with $c_{\text{Sn(II)}} = 0.01$ M and diffusion coefficient $D = 6.2 \times 10^{-6}$ cm² s⁻¹ yields the value: $Y_0 = 0.384$ S cm⁻² s^{0.5} [11], which is in good agreement with experimental data (Table 1, part a). Charge transfer resistance R_1 decreases from Cl⁻ to I⁻ and is indicative of the respective increase in i_0 . It follows from the latter variations that halides suppress the inhibitive effect of laprol in the above sequence. At the same time variations in double layer capacitance (element Q_{dl}) are not significant and do not show any exact interrelation with R_1 . In connection with the results obtained, it is reasonable to conclude that the introduction of

Table. Parameters of equivalent circuit $R_\Omega([R_1Q_1]Q_{dl}R_2)$ obtained for 0.01 M Sn(II) solutions containing 10 mg dm⁻³ of laprol and 30 μM of different halides. $R_\Omega = 0.3 \Omega \text{ cm}^2$.

Dimensions: $[E] = \text{V}$, $[R] = \Omega \text{ cm}^2$, $[Y_0] = \text{S cm}^{-2} \text{ s}^n$. Symbol * means an undetectably high value

Halide	E	R_1	Q_1		Q_{dl}		R_2
			$10^2 Y_0$	n	$10^6 Y_0$	n	
a) open-circuit conditions							
none	-0.24	5.2	37	0.492	30.0	0.920	*
Cl ⁻		3.0	39	0.486	24.4	0.963	*
Br ⁻		2.5	39	0.491	34.3	0.938	*
I ⁻		1.1	39	0.482	21.8	0.910	*
b) cathodically polarized electrodes							
Br ⁻	-0.28	80	1.16	0.369	30.0	0.931	*
	-0.30	900	0.017	0.712	27.8	0.929	-7620
	-0.32	2380	0.0021	0.921	22.4	0.944	-1750
	-0.35	1050	0.037	0.367	16.3	0.966	*
	-0.40	360	0.49	0.411	13.1	0.979	*
	-0.50	185	0.60	0.474	11.8	0.980	*

halides gives rise to the respective reconstruction of a double-layer structure. The high surface activity of halides is well known for different electrodes including Hg [18]. The competitive adsorption of laprol and halides might be responsible for the effects under discussion.

It should be emphasized that impedance characteristics strongly depend on the electrode potential (E). An example of experimental data shown in Fig. 5 is typical of all the halides. These data may be subdivided into two parts. The first of them corresponds to the region with the positive slope of voltammograms where impedance is described using the same equivalent circuit as above with the same physical sense of the elements listed in Table 1, part *b*. However, at E (-0.30 and -0.32 V), corresponding to the negative slope, some specification of equivalent circuit should be made. The negative impedance obtained in this region requires an additional negative resistance R_2 to be included. The presence of such element is indicative of the process strongly controlled by potential-dependent adsorption [19]. It should be noted that the factor n characterizing Q_1 deviates from the 0.5 value typical of Warburg impedance. This means that the applied equivalent circuit needs further refinement, despite the fact that it satisfactorily describes experimental data (Fig. 5). The ambiguity of equivalent circuits is a well-known property in impedance theory [17].

A decrease in double-layer capacitance with $|E|$ (element Q_{dl} in Table 1, part *b*) is clearly evident.

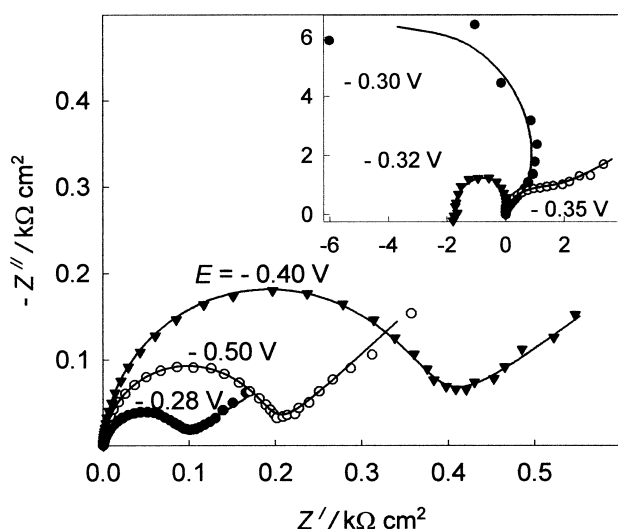


Fig. 5. Nyquist plots obtained at different electrode potentials (indicated at the curves) for 0.01 M Sn(II) solutions containing 10 mg dm⁻³ of laprol and 30 μM of bromide. Comparison of experimental (symbols) and simulated (solid lines) data. Parameters of equivalent circuit are listed in Table (part *b*)

However, Q_{dl} does not reach the values as low ($7\text{--}9 \mu\text{F cm}^{-2}$) as in the case of halide-free solutions [11].

The results obtained point clearly to a suppression of the inhibitive effect of laprol in the presence of halides, the action of which follows the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$. It is remarkable that halides initiate the opposite effects in the case of copper substrate [20]. This feature provides a great scope for the further improving of bronze plating, since the partial processes of copper and tin codeposition may be profitably controlled by the halides.

CONCLUSIONS

1. Impedance spectra obtained for halide- and/or laprol-containing Sn(II) solutions may be well-described using the equivalent circuit $R_{\Omega}([R_1Q_1]Q_{dl})$ involving ohmic resistance R_{Ω} , charge transfer resistance R_1 and constant phase elements Q_1 , Q_{dl} reflecting Warburg impedance and double layer capacitance respectively.

2. Halides Cl^- , Br^- and I^- exert no influence on impedance spectra in laprol-free solutions. In this case, Sn(II) electroreduction is mainly controlled by diffusion with exchange current density exceeding 0.1 A cm^{-2} .

3. Inhibitive adsorption of laprol was found to be partially suppressed by the halides in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$ due to competition among the adsorbates.

4. Negative impedance was detected in the region of the negative slope of voltammograms, where the double layer capacitance acquires the lowest value. However, this value is higher than in halide-free solutions.

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HALOGENIDŲ SLOPINAMA POLIETERIO LAPROLO 2402 C ADSORBCIJA ANT ALAVO ELEKTRODO

S a n t r a u k a

Taikant voltamperometrijos ir elektrocheminio impedanso spektroskopijos (EIS) metodus, ištirta polieterio laprolo 2402 C adsorbcinė elgsena ant alavo elektrodo labai rūgščiuose tirpaluose. Impedanso spektrus, gautus Sn(II) tirpaluose su halogenidais ir/arba laprolu, gerai aprašo ekvivalentinė grandinė $R_{\Omega}([R_1Q_1]Q_{dl})$, sudaryta iš ominės varžos R_{Ω} , krūvio pernešimo varžos R_1 ir pastoviosios fazės elementų Q_1 Q_{dl} , atspindinčių, atitinkamai, Warburgo impedansą ir dvigubą sluoksnio talpą. Halogenidai neturi jokios įtakos impedanso, išmatuoto tirpaluose be laprolo, spektrams. Priešingai, aptikta, kad halogenidai dalinai slopina inhibicinę laprolo adsorbciją sekoje: $Cl^- < Br^- < I^-$, vykstant konkurencijai tarp adsorbatų. Voltamperogramų neigiamo nuolinkio srityje užregistruotas neigiamas impedansas, įgyjantis žemiausią reikšmę, kuri vis dėlto yra didesnė negu tirpaluose be halogenidų.