

# Effect of Sn(II) on benzaldehyde adsorption on tin electrode in 1 M H<sub>2</sub>SO<sub>4</sub> solutions

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EIS data were obtained for tin electrode in 1 M H<sub>2</sub>SO<sub>4</sub> solutions containing milimolar amounts of benzaldehyde. It was found that the formation of adsorption layers was rather a slow process taking 2–3 hours till the stationary state was attained. However, Kramers–Kronig transforms show that in general the system remains sufficiently stable during one record of the impedance spectrum. The exception is Sn(II)-free solutions at short (less than 20 min) exposure times. Experimental impedance spectra can be quantitatively described with high accuracy (frequency error is less than 2%) by means of  $R_{\Omega}(Q_{dl}[R_{ad}C_{ad}W_{ad}][R_{ct}Q_d])$  equivalent circuit containing both adsorption and charge transfer parameters. The analysis of their dynamics show that the adsorption layers are more mobile in the presence of Sn(II) and the reversibility of the adsorption-desorption processes is higher in this case.

**Key words:** tin, benzaldehyde, adsorption, impedance

## INTRODUCTION

The plating bath intended for the electrodeposition of tin and its alloys contain generally surface-active substances (SAS) that suppress the growth of dendrites, increase a throwing power of electrolytes and can operate as brighteners. Various derivatives of benzene are also used for this purpose [1–7]. Their high surface activity often manifests itself in co-adsorption with other SAS [1]. Sometimes the adsorption processes are accompanied by the destruction of additives with the following incorporation of their fractions into the coatings [2]. It should be also mentioned that some of them (aromatic aldehydes and ketones) could be reduced in a certain region of potentials [3, 4] yielding, for instance, aromatic alcohols that can be also classified as SAS [5].

Different mechanisms of SAS influence on Sn(II) reduction have been discussed. According to [6], strong inhibitive adsorption could significantly decrease the number of active sites on tin surface and result in a more uniform distribution of the current density. Another mechanism supposes the formation of an adsorption barrier that retards the penetration of Sn<sup>2+</sup> ions into the tin surface. The possibility of the formation of adsorption layers exhibiting the properties of membranes has also been analyzed [7].

Benzaldehyde (BA) is one of the substances that are known for being effective brighteners in tin plating.

Though there is some information for the most part concerning the technological aspects, more exhaustive data on BA adsorption behavior are still desired. In our opinion, one of topical questions involves a comparison of BA surface activity in Sn(II)-free and Sn(II)-containing solutions. In this connection, we undertook the present investigation preferring the method of electrochemical impedance spectroscopy (EIS) that makes it possible to obtain some extensive information on both faradaic and non-faradaic processes.

## EXPERIMENTAL

The solutions under investigation contained 1 M H<sub>2</sub>SO<sub>4</sub> (high purity), 0.01 M SnSO<sub>4</sub> (Fluka, Germany) and different amounts of benzaldehyde (Aldrich, Germany). Thrice-distilled water was used for the preparation of solutions that were deaerated with an argon stream over 0.5 h.

An electrochemical cell equipped for the EIS measurements was used. A Pt wire with a surface area of 0.36 cm<sup>2</sup> served as a substrate for the preparation of the working electrode. It was coated at 10 mA cm<sup>-2</sup> with ~2 μm thick copper sub-layer in a solution containing (g dm<sup>-3</sup>): CuSO<sub>4</sub>·5 H<sub>2</sub>O – 200 and H<sub>2</sub>SO<sub>4</sub> – 50. Then 5–7 μm of a smooth tin coating was deposited at 10 mA cm<sup>-2</sup> in the solution containing (g dm<sup>-3</sup>): SnSO<sub>4</sub> – 50, H<sub>2</sub>SO<sub>4</sub> – 160 and SAS sintanol – 1. The working electrodes were carefully rinsed with water, immediately immersed into the solution under investigation and kept in it for a controlled time τ. Platinum cylinder (~6 cm<sup>2</sup>)

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was used as an auxiliary electrode for the polarization with an alternating current. A conventional Ag|AgCl|KCl(sat) reference electrode was used. Electrode potentials were converted to the standard hydrogen scale. All experiments were performed at 20 °C.

The impedance spectra were obtained within a frequency  $f$  range from 0.1 Hz to 50 kHz using a Zahner Elektrik (Germany) IM6 impedance spectrum analyzer. The open-circuit potential was maintained during the measurements. A sufficiently low (5 mV) amplitude of the alternating voltage was applied. Each record started at the maximum frequency and took 4–5 min. Computer programs elaborated by Boukamp [8] were used for analyzing the impedance data. Other details concerning EIS measurements are available in [9–11].

## RESULTS AND DISCUSSION

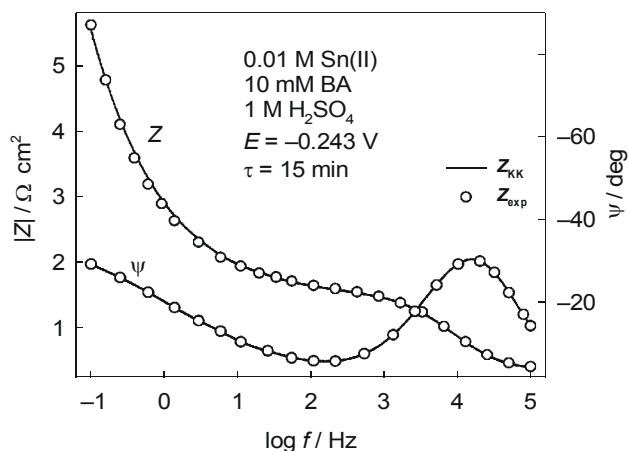
EIS data obtained for BA containing solutions show some properties that are also typical of other SAS widely used in tin-plating baths. Various polyethers should be mentioned in this connection. The general peculiarity lies in the fact that the adsorption of these SAS is rather slow. The impedance data obtained in the presence of sintanol DS-10 [10], oligomers of ethyleneglycol [11] as well as BA depend on the Sn-electrode exposure time  $\tau$  in the solutions. Impedance (hence, the adsorption parameters as well) can slowly vary within 2–3 hours when ultimately the stationary state is attained.

Since BA adsorption varies with time, it is necessary to ascertain how this can distort the impedance data. It must be said that the record of the major part of the spectra (at  $f > 10$  Hz) takes only some ten seconds. Therefore, minor deviations in the estimated adsorption parameters might be expected. However, in order to verify the impedance data, we made use of Kramers–Kronig transforms. This is a general mathematical procedure that allows to check whether the following constraints are satisfied: linearity of the system, causality, stability and finiteness [12, 13]. The real part of impedance ( $Z'$ ) can be obtained from an imaginary component ( $Z''$ ) and vice versa, according to the equations:

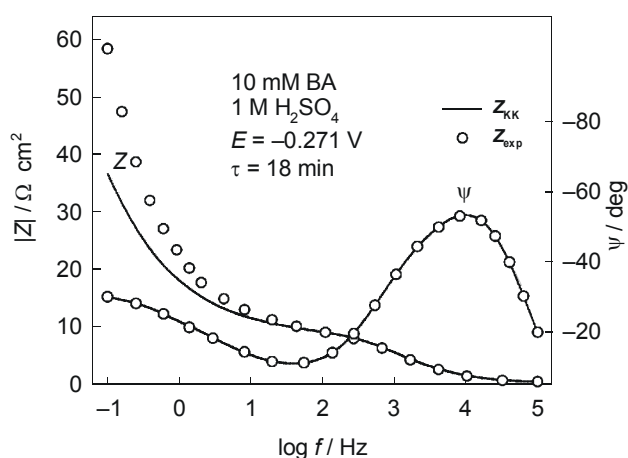
$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_0^{\infty} \frac{x Z''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx, \quad (1)$$

$$Z''(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx. \quad (2)$$

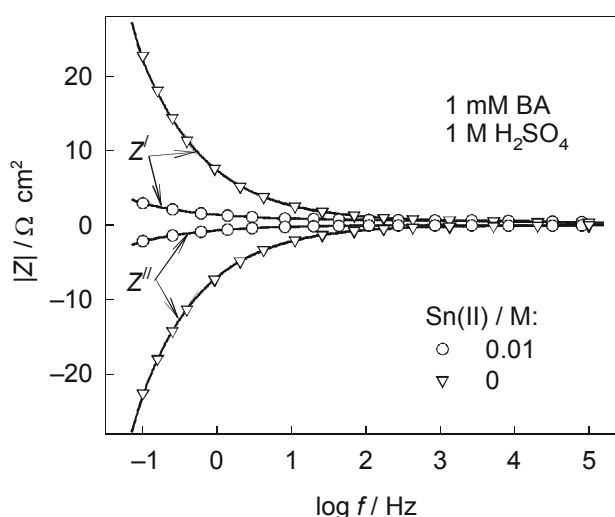
A typical example of such transform is demonstrated in Fig. 1. It can be seen that both the transformed modulus of impedance and the one obtained experimentally coincide very well. The same holds true for the phase angle  $\psi$  as well. The overwhelming majority of the obtained results is of the same character that is indicative of a sufficient stability of the system during



**Fig. 1.** Comparison of impedance ( $Z$ ) and phase angle ( $\psi$ ) spectra obtained from Kramers–Kronig transforms (lines) with respective experimental data (symbols) obtained for the solution of the indicated composition



**Fig. 2.** The same as in Fig. 1 in Sn(II)-free solution



**Fig. 3.** Experimental (symbols) and simulated (lines) impedance spectra of Sn electrode that was exposed for 100 minutes to the solutions containing 1 mM of benzaldehyde, 1 M of sulphuric acid and Sn(II) as indicated

the measurement. A rather rare case when both  $|Z|$  spectra (transformed and measured immediately) differ is given in Fig. 2. Such a phenomenon is observed only for short exposure times in Sn(II)-free solutions. It is notable that a certain instability has no effect on  $\psi$  spectrum. It seems that the surface available for adsorption somewhat diminishes in time. A comparison of Figs. 1 and 2 would also demonstrate that the formation of the adsorption layer becomes more vigorous in the presence of Sn(II).

The second general property of SAS adsorption may be seen from Fig. 3, where the impedance spectra obtained at the same exposure time are compared. It is evident that both real and imaginary components of impedance are ca tenfold higher in the case of Sn(II)-free solutions. Special experiments showed that this could not result from a difference in the open-circuit potentials that are equal to  $-0.242$  V (Sn(II) solutions) and  $-0.269$  V (Sn(II)-free ones). The first of them is actually the equilibrium potential of Sn-electrode [10, 11], whereas the other quantity should be treated as the corrosion potential. It must be emphasised, however, that Sn corrosion in highly acidic solutions is very weak and its kinetics may be easily omitted from consideration of the impedance data [14].

The main reason of this effect lies in the redox process involving Sn(II). It proceeds with a rather high exchange current density ranging into tens of mA cm<sup>-2</sup>. Most impedance data can be described quantitatively with high accuracy (frequency error does not exceed 1–2%) by means of equivalent circuit, whose description code is  $R_{\Omega}(Q_{dl}[R_{ad}C_{ad}W_{ad}][R_{ct}Q_d])$ . According to Boukamp [8], the elements in series are given in square brackets and the parallel-connected elements are enclosed in parenthesis. This circuit contains the ohmic resistance of the solution ( $R_{\Omega}$ ), the elements representing the adsorption of SAS ( $R_{ad}$ ,  $C_{ad}$ ,  $W_{ad}$ ), constant phase elements (CPE) representing the electric properties of double electric layer ( $Q_{dl}$ ) and diffusive mass transport of Sn(II) ( $Q_d$ ). The sub-circuit  $[R_{ct}Q_d]$  containing both  $Q_d$  and charge transfer resistance  $R_{ct}$  should be deleted when the impedance in Sn(II)-free solutions is analysed.

The quantities used to describe of the data given in Fig. 3 are listed in Table. According to the impedance theory [12], the admittance  $Y$  of CPE is defined by the relationship

$$Y = Y_0(j\omega)^n, \quad (3)$$

Table. Magnitudes of elements of equivalent circuit  $R_{\Omega}(Q_{dl}[R_{ad}C_{ad}W_{ad}][R_{ct}Q_d])$

Element →	$R_{\Omega}$	$Q_{dl}$		$R_{ad}$	$C_{ad}$	$W_{ad}$	$R_{ct}$	$Q_d$	
↓ $c_{Sn(II)}$	$R$	$10^6 Y_0$	$n$	$R$	$C$	$Y_0$	$R$	$Y_0$	$n$
0	0.33	55.8	1.00	0.13	1.35	0.04	–	–	–
10	0.32	38.2	0.97	0.85	0.0045	0.10	0.30	0.39	0.49

Dimensions:  $[c] = \text{mM}$ ,  $[R] = \Omega \text{ cm}^2$ ,  $[Y_0] = \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$ ,  $[C] = \text{F cm}^{-2}$ .

where  $\omega = 2\pi f$  and  $j = \sqrt{-1}$ . The dimensionless exponent  $n$  characterises the nature of CPE. It transforms into capacitance  $C$  or Warburg impedance  $W$  at  $n$  being equal to 1 and 0.5, respectively. Thus,  $Q_{dl}$  may be treated as an effective capacitance and  $Q_d$  is actually the diffusion impedance (see Table). The theoretical value of  $Y_0$  for this CPE,  $0.384 \Omega^{-1} \text{ cm}^{-2} \text{ s}^{0.5}$  [10], is in good agreement with the experimental quantity. It can be seen from the example given in Table that the addition of Sn(II) affects mainly the adsorption elements.

The addition of Sn(II) has little effect on the double layer capacitance. The main difference consists in the dynamics of  $C_{dl}$  that is more pronounced in the case of Sn(II)-containing solutions (Fig. 4). On the whole, a decrease in  $C_{dl}$  is usually related with an increase in the surface concentration of SAS.

The presence of  $[R_{ad}C_{ad}W_{ad}]$  sub-circuit shows that the formation of an adsorption layer proceeds with a finite rate that is conditioned by both diffusion and adsorption steps. It follows from [15, 16] that the product of  $R_{ad}C_{ad}$  represents the kinetic relaxation time  $\tau_k$  that, in its turn, is determined by the adsorption rate. This time is significantly higher in the case of Sn(II)-free solutions. Besides, its variation with time is more pronounced (Fig. 5). When the adsorption obeys the Frumkin isotherm,  $\tau_k$  is the reciprocal of the adsorption exchange rate  $v_0$  [17]. Thus, a conclusion can be drawn that the adsorption layers are more mobile in the

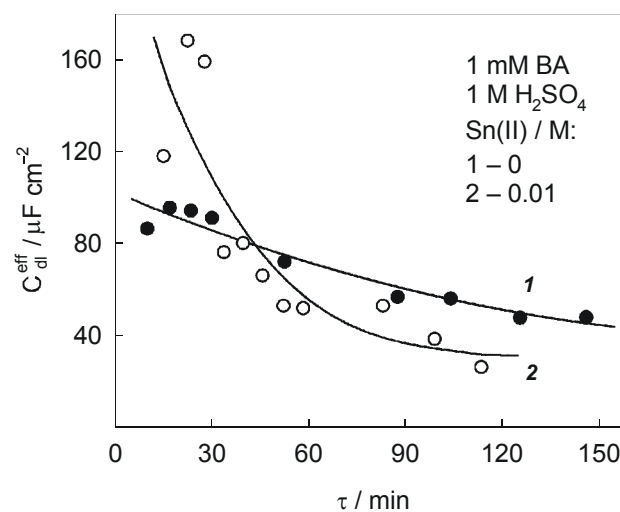
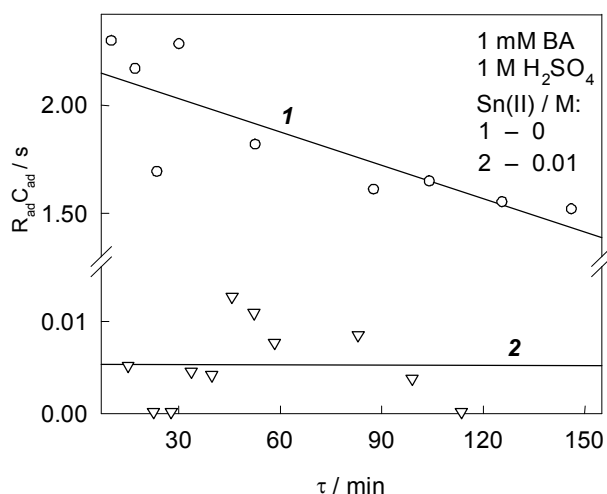


Fig. 4. Variations of the effective double-layer capacitance with time in the solutions of indicated composition



**Fig. 5.** Variations of  $R_{ad}C_{ad}$  product with time in the solutions of indicated composition

presence of Sn(II) and the reversibility of the adsorption-desorption processes is higher in this case.

The values of  $Y_{ow}$  that characterize the element  $W_{ad}$  remain of the same order after Sn(II) is added (Fig. 6). It is necessary to say that mathematical expressions of  $Y_{ow}$  are more complicated than these describing the diffusive mass-transport of discharging ( $Sn^{2+}$ ) ions. This first quantity is in complicated relationships with other adsorption parameters and elements of the equivalent circuit [16–18] that makes its analysis rather problematic.

## CONCLUSIONS

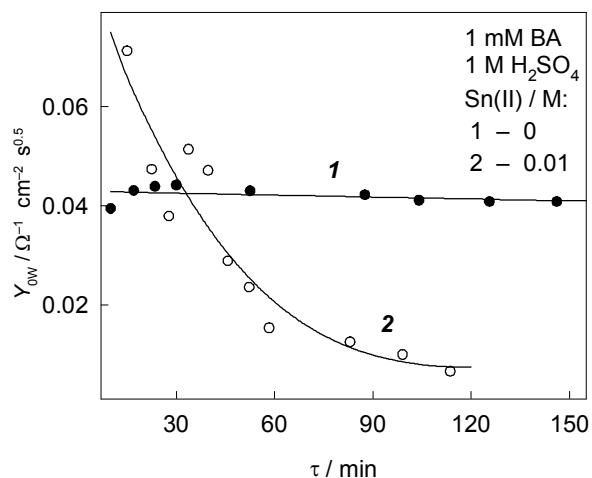
1. According to the EIS data obtained for tin electrode in highly acidic solutions containing benzaldehyde, the formation of an adsorption layer is rather slow. The adsorption parameters can vary within 2–3 hours till the stationary state is attained.

2. Kramers–Kronig transforms show that, in general, the system remains sufficiently stable during one record of the impedance spectrum. The exception is Sn(II)-free solutions at short (less than 20 min) exposure times.

3. Experimental impedance spectra can be quantitatively described with high accuracy (frequency error is less than 2%) by means of general equivalent circuit, the description code of which is  $R_{\Omega}(Q_{dl}[R_{ad}C_{ad}W_{ad}][R_{ct}Q_{dl}])$ .

4. The adsorption layers are more mobile in the presence of Sn(II) and the reversibility of the adsorption-desorption processes is higher in this case.

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**Fig. 6.** Variations of Warburg conductance with time in the solutions of indicated composition

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**SN(II) ĮTAKA BENZALDEHIDO ADSORBCINEI  
GEBAI ANT ALAVO ELEKTRODO 1 M H<sub>2</sub>SO<sub>4</sub>  
TIRPALUOSE**

**S a n t r a u k a**

Elektrocheminės impedanso spektroskopijos metodu ištirta benzaldehydo (BA) adsorbcija ant alavo elektrodo 1 M H<sub>2</sub>SO<sub>4</sub> tirpaluose su milimoliariniais BA kiekiais. Nustatyta, kad adsorbciniai sluoksniai formuojasi labai lėtai ir reikia 2–3 valandų,

kad būtų pasiekta stacionarioji būseną. Tačiau Kramerio–Kronigo transformacijos rodo, kad impedanso spektro užrašo metu sistemos išlieka pakankamai stabilios, išskyrus trumpų (<20 min) ekspozicijų atvejus tirpaluose be Sn(II). Eksperimentinius impedanso spektrus galima aprašyti kiekybiškai su aukštu tikslumu (dažnuminė paklaida yra mažesnė už 2%), naudojant ekvivalentinę grandinę  $R_t(Q_{dl}[R_{ad}C_{ad}W_{ad}][R_{ct}Q_{dl}])$ , kurioje yra ir krūvio pernašos, ir adsorbcijos parametrai. Jų analizė parodo, kad Sn(II) tirpaluose susidaro judresni adsorbciniai sluoksniai, o adsorbcijos–desorbcijos procesų grįžtamumas šiuo atveju yra didesnis.