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INHIBITORY EFFECT OF SOME AMINO ACIDS ON COPPER ELECTRODEPOSITION FROM ACID BATHS

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In this paper, the possibility of using glycocoll, DL-alanine and L-phenylalanine as leveling and brightening agents in the copper electrodeposition has been investigated. Information about the influence of above-mentioned compounds have been obtained using linear sweep voltammetry. Kinetic parameters, exchange current density, and transfer coefficient were evaluated by Tafel slope method between 22°C and 60°C. Electrochemical behavior of glycocoll, DL-alanine and L-phenylalanine has been studied by cyclic voltammetry on platinum, and adsorption Gibbs free energy has been determined using Langmuir isotherm. The morphology of copper deposits has been examined by optical microscopy.

Keywords: copper electrodeposition, Tafel slope method, Langmuir isotherm

1. Introduction

The electrodeposition of copper is widely applicable nowadays to realize protective or intermediate copper layers. Until now, best results have been accomplished using cyanide baths, because obtained layers are more compact, adherent and bright. Taking into account that the European legislation requires a restriction of cyanide baths, especially because of its environmental problems, an alternative solution to obtain copper deposits of the same quality from non-cyanide baths such as those based on $CuSO_4$ and H_2SO_4 have been considered [1]. In order to obtain adherent, compact and bright deposits from this kind of baths it is necessary to use some additives as cathodic process inhibitors [2]. In the literature, a huge number of substances used as brighteners and leveling agents have been proposed: natural compounds [3], sodium lauryl sulphate, saccharin, 1,2,3-benzotriazole [4], dyes as Basic Red 12 [5], some alcohols e.g. polyethylene glycol [6] and hydroxyethylated 2-butyne-1,4-diol [7], sulfonic acids, e.g. mercapto-2-propanesulphonic acid [6] and 3-mercapto-1-propanesulfonate [8], gelatin [9], Bitrex (denatonium benzoate) [9], phenol sulphonic acid [10], but also some pharmaceutical drugs [11].

The aim of this paper is the identification of some non-toxic and environmentally friendly leveling agents. That is the reason why the research was focused on the use of some available amino acids, glycocoll (Gly), DL-alanine

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(Ala) and L-phenylalanine (Phe), as leveling and brighteners in copper deposition acid baths.

2. Experimental part

2.1. Materials and equipment

Materials used during the experiment were: $CuSO_4{\cdot}5H_2O$, ≥98%, Merck; Sulfuric acid 96% Suprapur®, Merck; glycocoll, ≥ 99.7%, Merck; L-phenylalanine, 99%, Sigma-Aldrich and DL-alanine 99%, Sigma-Aldrich.

Supporting electrolyte solution (SES) contains an amount of 150 g L^{-1} $CuSO_4{\cdot}5H_2O$ (38 g L^{-1} Cu^{2+}) and 40 g L^{-1} H_2SO_4, and solutions with inhibitor contain a concentration of 10^{-2} mol L^{-1} amino acid (Gly, Ala, Phe) for linear voltammetry and different concentration ($10^{-4} \div 10^{-2}$) in the experiments on Gibbs free energy determination.

Cyclic voltammograms have been drawn using a Potentiostat/Galvanostat Autolab 128N Metrohm, in a thermostatic undivided electrochemical cell equipped with a copper working electrode, two graphite rods as a counter electrode and Ag/AgCl as a reference electrode.

Information about the surface morphology was obtained by using an optical metallographic microscope Optika B510MET.

2.2. Calculation methods

Kinetic parameters, exchange current density i_o and cathodic transfer coefficient ($1\text{-}\alpha$), were determined by Tafel polarization method, at different temperatures: 298, 303, 313, 323 and 333 K. Further, the activation energy E_a for the copper electrodeposition was calculated using Arrhenius plot $\lg i_o = f(T^{-1})$, and Gibbs free energy for the adsorption process was obtained by Langmuir isotherms.

3. Results and Discussion

3.1. Cyclic voltammetry

In Figs. 1-3, cyclic voltammograms recorded on Pt electrode in a 40 g L^{-1} H_2SO_4 solution, at room temperature, in the presence and in the absence of the amino acids are shown. In the anodic range, on above mentioned voltammograms, it can be observed only the wave corresponding to the oxygen evolution reaction. If the potential is shifted towards negative potentials, peaks corresponding to H atoms and H_2 molecules adsorption may be remarked. At advanced cathodic polarization, hydrogen evolution occurs. Further, at the anodic shift of the potential, oxidation peaks of hydrogen species are perceptible.

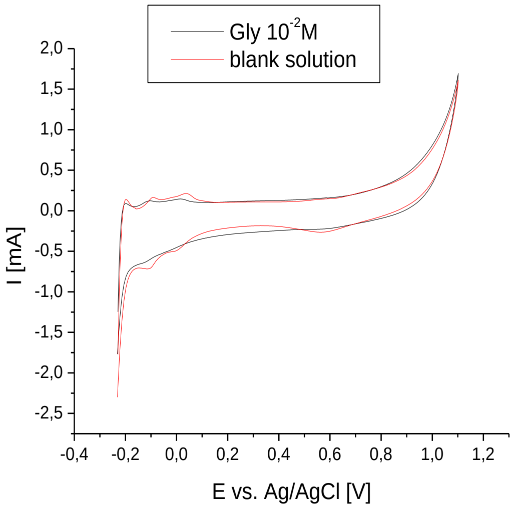


Fig. 1. Cyclic voltammograms in 40 g L^{-1} H_2SO_4 solution without and with 10^{-2} mol L^{-1} Gly, scan rate of 100 mV s^{-1}.

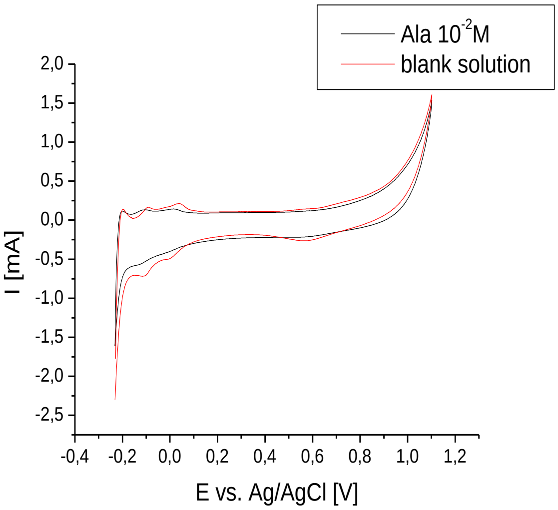


Fig. 2. Cyclic voltammograms in 40 g L^{-1} H_2SO_4 solution without and with 10^{-2} mol L^{-1} Ala, scan rate of 100 mV s^{-1}.

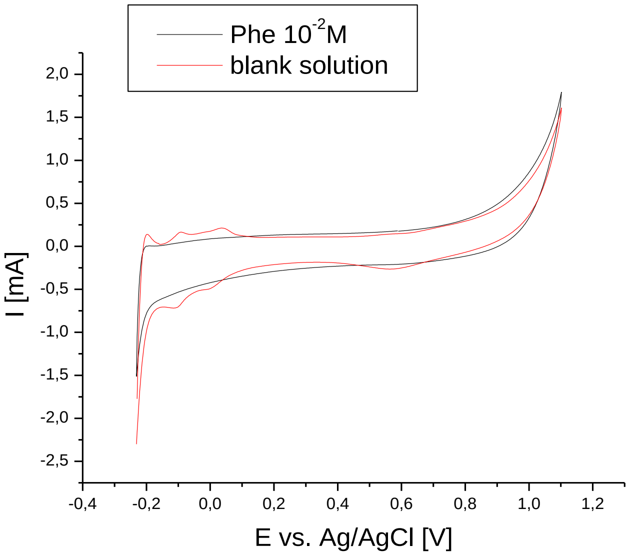


Fig. 3. Cyclic voltammograms in 40 g L^{-1} H_2SO_4 solution without and with 10^{-2} mol L^{-1} Phe, scan rate of 100 mV s^{-1}.

Finally, voltammograms presented in Figs. 1-3 show that the amino acids Gly, Ala and Phe are stable in the aqueous solution of H_2SO_4, in a range of potential between hydrogen and oxygen evolution reactions. Moreover, the amino acids will be stable in copper deposition baths containing $CuSO_4$ and H_2SO_4, taking into account that hydrogen evolution occurs are appreciably more positive that potential of copper ionization process.

3.2. Tafel linear polarization

In order to determine the activation energy E_a for the copper electrodeposition, cathodic linear voltammograms have been drawn in SES in the absence and presence of 10^{-2} mol L^{-1}, at the following temperatures: 298, 303, 313, 323 and 333 K. Firstly, kinetic parameters - exchange current density i_o and cathodic transfer coefficient (1-α) - were calculated by Tafel polarization method, results been given in Table 1. Using exchange current densities values at different temperatures, activation energy has been evaluated based on the graphical representation (Fig. 4) of the Arrhenius equation (1).

$$\log i_o = \frac{-E_a}{2.303RT} + A \tag{1}$$

Activation energies are given in Table 1.

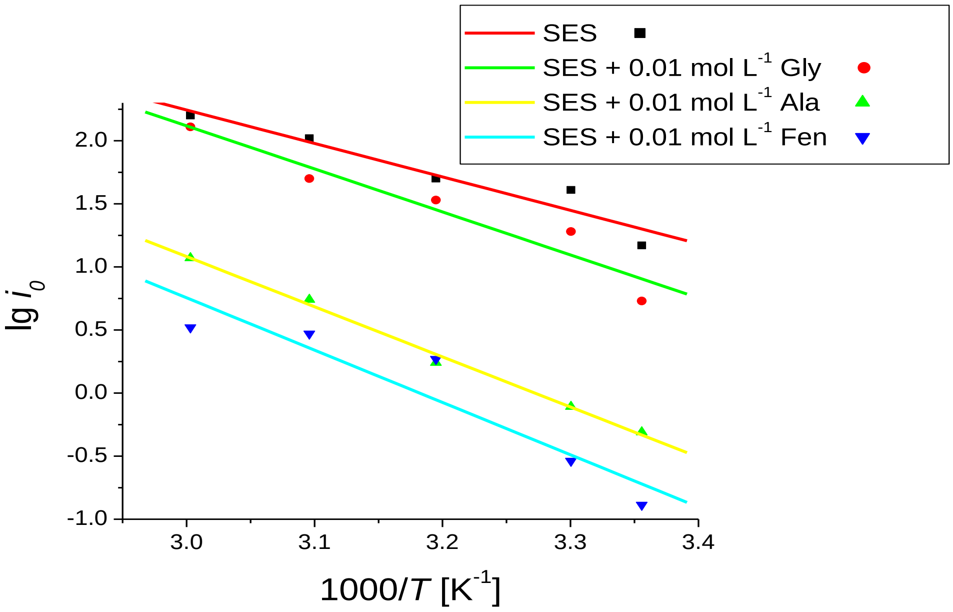


Fig. 4. Arrhenius plots for SES without additive, respectively for solutions with 10^{-2} mol L^{-1} Gly, Ala and Phe.

The values of current density i_o and transfer coefficients $1-\alpha$, determined in SES, are similar with those reported in the literature [12].

Table 1.

Values of E_a , lg i_o *and* $(1-\alpha)$ for SES without additive and with 10^{-2} mol L^{-1} Gly, Phe, Ala.

Electrolyte solution	*T* [K]	i_o [A m^{-2}]	1-α	E_a [kJ mol^{-1}]
SES + 0.01 mol L^{-1} Gly	298	5.37	0.27	61.1
	303	19.05	0.22	
	313	33.88	0.24	
	323	50.12	0.26	
	333	128.82	0.29	
SES + 0.01 mol L^{-1} Ala	298	0.49	0.29	68.1
	303	0.78	0.26	
	313	1.74	0.29	
	323	5.50	0.29	
	333	11.75	0.33	
SES + 0.01 mol L^{-1} Phe	298	0.13	0.21	79.5
	303	0.29	0.29	
	313	1.86	0.22	
	323	2.95	0.24	
	333	3.31	0.30	
SES	298	14.79	0.22	48.5
	303	40.74	0.20	
	313	50.12	0.21	
	323	104.71	0.22	
	333	158.49	0.21	

In the presence of Gly, Ala and Phe, transfer coefficients ($1-\alpha$), does not undergo substantial changes, whereas the exchange current density i_o significantly diminished as consequence of the amino acids inhibitory properties. As it is expected, the most powerful effect is given by Phe.

The increasing of the activation energy E_a for the cathodic copper deposition is another evidence of amino acids inhibitory effect. The more is the activation energy, the more is the inhibition capacity of the amino acids. Consequently, Phe is more efficient as levelling agent for copper deposition than Ala and Gly. Certainly, there is a direct dependence between the inhibition capacity of amino acids and their corresponding molecular volume.

3.3. Langmuir adsorption isotherm

In order to obtain information about the interaction nature between amino acids molecules and metal surface, the adsorption Gibbs free energy have been calculated using Eq. (2) [13].

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5K_{ads}) \quad (2)$$

where R is gas constant (8.314 J mol^{-1} K^{-1}); K_{ads} - adsorption equilibrium constant and T - thermodynamic temperature, K.

According to the literature data [15], the adsorption equilibrium constant was calculated from by the Langmuir linear dependence of c_{inh}/θ as a function of c_{inh}, given by the Eq. (3).

$$\frac{c_{inh}}{\theta} = \frac{1}{K_{ads}} + c_{inh} \tag{3}$$

where c_{inh} is the inhibitor concentration in the electrolyte solution, and θ is the surface coverage calculated with the help of the relationship (4) [13].

$$\theta = \frac{|i| - |i_{inh}|}{|i|} \tag{4}$$

where i is the cathodic current density in the absence of the inhibitor, and i_{inh} - current density in the presence of the inhibitor.

Experimentally, the linear dependence $c_{inh}/\theta = f(c_{inh})$, revealed in Fig. 5, was determined based on the data obtained using Tafel slope method (Table 2).

Table 2

Values of the ΔG^{o}_{ads} and the type of adsorption for studied inhibitors.

Solution	c_{inh} [mol L^{-1}]	θ	i [A m^{-2}]	c_{inh}/θ [mol L^{-1}]	ΔG^{o}_{ads} [kJ mol^{-1}]	Type of adsorption
Gly	0	0	$1.37 \cdot 10^{-5}$	0	-35.5	Predominant chemical
	10^{-4}	0.87	$1.77 \cdot 10^{-6}$	$1.15 \cdot 10^{-4}$		
	$5 \cdot 10^{-4}$	0.90	$1.33 \cdot 10^{-6}$	$5.54 \cdot 10^{-4}$		
	10^{-3}	0.90	$9.53 \cdot 10^{-7}$	$1.10 \cdot 10^{-3}$		
	$5 \cdot 10^{-3}$	0.98	$6.81 \cdot 10^{-8}$	$5.00 \cdot 10^{-3}$		
	0.01	0.99	$4.98 \cdot 10^{-8}$	10^{-2}		
Ala	0	0	$1.37 \cdot 10^{-5}$	0	-25.6	Predominant physical
	$5 \cdot 10^{-4}$	0.23	$1.06 \cdot 10^{-5}$	$2.23 \cdot 10^{-3}$		
	10^{-4}	0.06	$1.01 \cdot 10^{-5}$	$1.90 \cdot 10^{-3}$		
	10^{-3}	0.39	$6.28 \cdot 10^{-6}$	$2.60 \cdot 10^{-3}$		
	$5 \cdot 10^{-3}$	0.84	$1.01 \cdot 10^{-6}$	$5.96 \cdot 10^{-3}$		
	0.01	0.98	$1.05 \cdot 10^{-8}$	10^{-2}		
Phe	0	0	$1.37 \cdot 10^{-5}$	0	-25.7	Predominant physical
	10^{-4}	0.05	$1.31 \cdot 10^{-5}$	$2.20 \cdot 10^{-3}$		
	$5 \cdot 10^{-4}$	0.14	$1.18 \cdot 10^{-5}$	$3.50 \cdot 10^{-3}$		
	10^{-3}	0.19	$1.11 \cdot 10^{-5}$	$5.30 \cdot 10^{-3}$		
	$5 \cdot 10^{-3}$	0.25	$1.03 \cdot 10^{-5}$	$1.98 \cdot 10^{-2}$		
	0.01	0.26	$9.63 \cdot 10^{-6}$	$3.79 \cdot 10^{-2}$		

The value of the free Gibbs energy shows if the inhibitor adsorption on the metal surface is physical or chemical. If free Gibbs energy is about - 40 kJ mol^{-1}, the adsorption is a chemical process, i.e. a strong bond between metal and organic substrate, respectively physical (weak interaction) if it is about -20 kJ mol^{-1} [14].

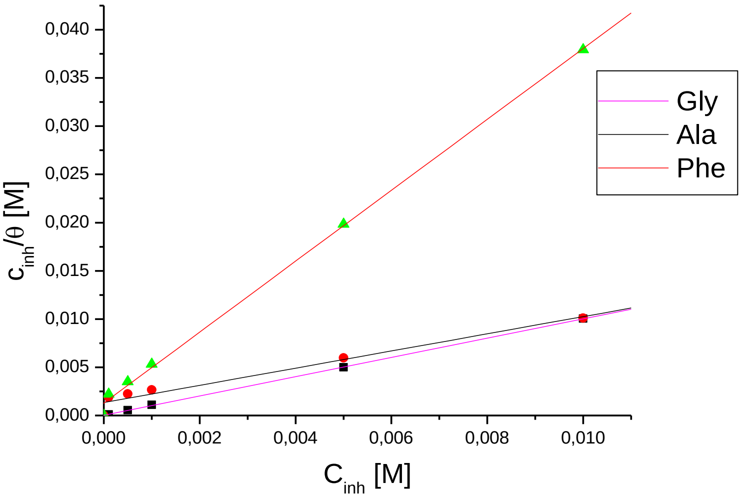


Fig. 5. Langmuir adsorption isotherm for the solution with Gly, Ala and Phe as inhibitors.

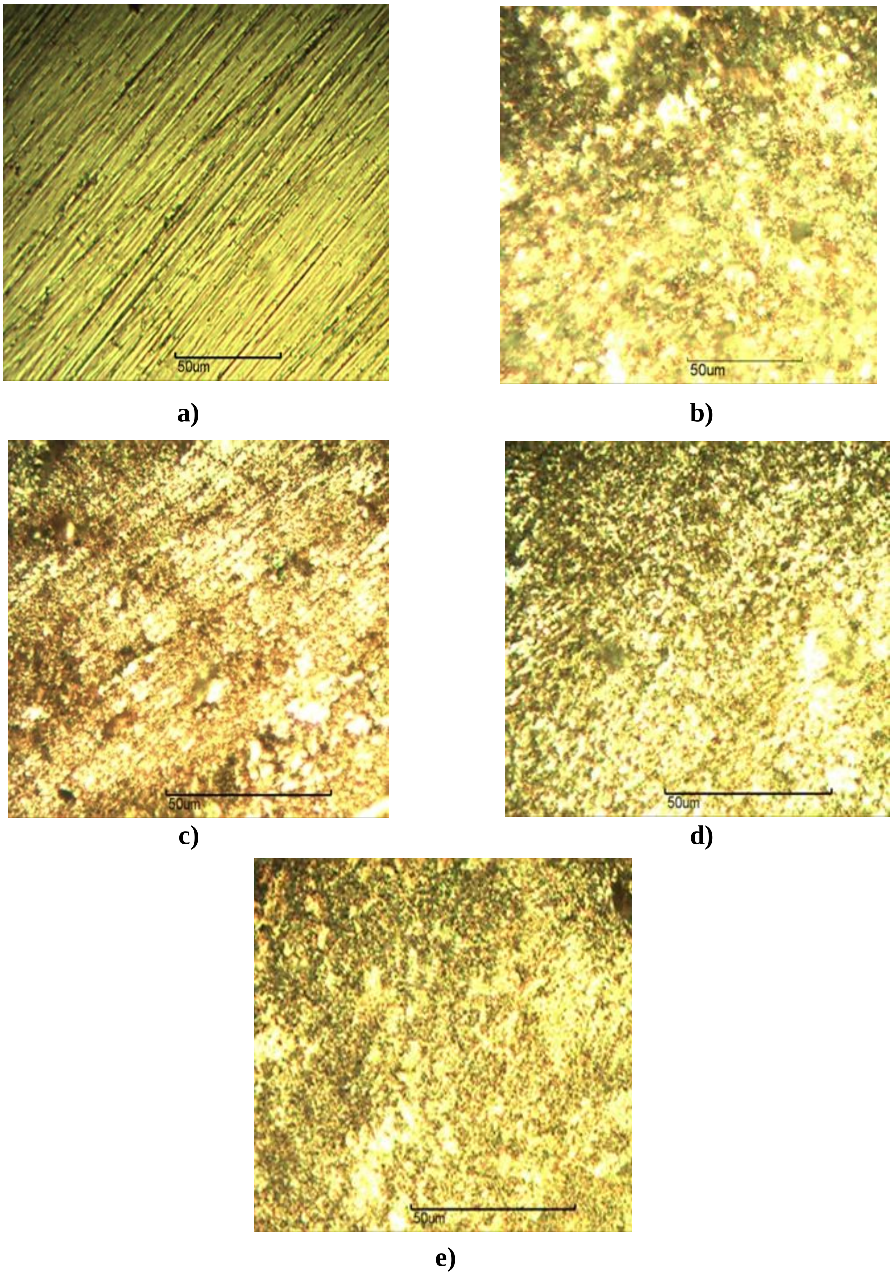
It can be concluded that for glycocoll the adsorption is predominantly chemical, for L-phenylalanine and DL-alanine the adsorption is predominantly physical in both cases.

3.4. Surface morphology analysis

Information about the surface morphology were obtained using a metallographic microscope Optika B510MET. Electrodeposited copper layer has been obtained by chrono-potentiometry at a current density of 100 A m^{-2}, during 10 minutes, in SES at room temperature. Further, the electrode has been cleaned up and degreased. The microscope images obtained are shown in the Fig. 6.

Analyzing the obtained images, it can be noticed that the deposition of copper in the presence of Phe (Fig. 6e) is smoother and the surface is more uniformly covered than in the presence of Ala (Fig. 6d), respectively of Gly (Fig. 6c). This is due to the high value of E_a for the copper electrodeposition process in presence of Phe, as a consequence of a the higher molecular volume and surface coverage. The deposition without inhibitor (Fig. 6b) has the weakest quality, that being the reason why it is really necessary to use levelling additives.

Although, the interaction between Gly and metal (predominantly chemical) is stronger than the interaction Ala – metal or Phe – metal (predominantly physical), the inhibitory effect of Gly in the cathodic copper deposition from acid baths is not powerful that of Ala and Phe, because the molecular volume of Ala and Phe is significantly larger that of Gly.



a) **b)**

c) **d)**

e)

Fig. 6. Microscope images of the surfaces: a) surface before the electrodeposition, b) electrodeposition in SES, c) electrodeposition in SES + Gly 10^{-2} mol L^{-1}, d) deposition in SES + Ala 10^{-2} mol L^{-1}, e) electrodeposition in SES + Phe 10^{-2} mol L^{-1}.

4. Conclusions

From cyclic voltammograms it can be observed that glycocoll (Gly), DL-alanine (Ala) and L-phenylalanine alanine (Phe) do not undergo any transformations (oxidation or reduction) in the electrode potential ranges of copper electrodeposition from acid baths.

Linear sweep voltammetry data allowed the evaluation of the activation energy of copper deposition process in the supporting electrolyte solution in the absence and presence of amino acids. It could be noted that the activation energy is increasing with the molecular weight of the inhibitor, and consequently, Phe is more efficient inhibitor than Ala or Gly. Therefore, it is expected that Phe will be a better levelling agent in the copper deposition bath.

Free Gibbs energies calculated by Langmuir adsorption isotherm have shown that the interaction between metal and Phe (-25,7 kJ/mol) or Ala (-25,6 kJ/mol) is predominantly physical, whereas that between metal and Gly (-35,5 kJ/mol) is predominantly chemical.

Optical micrographs revealed that all three studied amino acids could be successfully used as inhibitors in the electrodeposition process of copper from acid baths.

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