

VILNIUS UNIVERSITY
INSTITUTE OF CHEMISTRY OF CENTER FOR
PHYSICAL SCIENCES AND TECHNOLOGY

Virginija Kepenienė

**INVESTIGATION OF PECULIARITIES OF ELECTROLESS COPPER
PLATING SYSTEMS USING HYDROXYCARBOXYLIC ACIDS AS Cu(II)
LIGANDS**

Summary of Doctoral Dissertation
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Vilnius 2012

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Scientific supervisor:

Prof. Dr. Habil. Eugenijus Norkus (Center for Physical Sciences and Technology, Physical Sciences, Chemistry – 03P)

Doctoral dissertation is defended at the Evaluation board of Chemistry of Vilnius University:

Chairman:

Prof. Dr. Habil. Aivaras Kareiva (Vilnius University, Physical Sciences, Chemistry – 03P)

Members:

Prof. Dr. Habil. Albertas Malinauskas (Center for Physical Sciences and Technology, Physical Sciences, Chemistry – 03P)

Prof. Dr. Habil. Audrius Padarauskas (Vilnius University, Physical Sciences, Chemistry – 03P)

Assoc. Prof. Dr. Ingrida Ancutienė (Kaunas University of Technology, Physical Sciences, Chemistry – 03P)

Assoc. Prof. Dr. Jūratė Senvaitienė (P.Gudynas Center for Restoration, Physical Sciences, Chemistry – 03P)

Official Opponents:

Assoc. Prof. Dr. Audronė Gefenienė (Lithuanian University of Educational Sciences, Physical Sciences, Chemistry – 03P)

Dr. Loreta Tamašauskaitė-Tamašiūnaitė (Center for Physical Sciences and Technology, Physical Sciences, Chemistry – 03P)

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Address: A. Goštauto 9, LT-01108, Vilnius, Lithuania

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The doctoral dissertation is available at the Library of Institute of Chemistry and at the Library of Vilnius University.

VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO
CHEMIJOS INSTITUTAS

Virginija Kepenienė

**CHEMINIO VARIAVIMO SISTEMŲ, Cu(II) LIGANDAIS NAUDOJANT
HIDROKSIKARBOKSIRŪGŠTIS, YPATUMŲ TYRIMAS**

Daktaro disertacijos santrauka
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Mokslinis vadovas:

Prof. habil. dr. Eugenijus Norkus (Fizinių ir technologijos mokslų centras, fiziniai mokslai, chemija – 03 P)

Disertacija ginama Vilniaus universiteto Chemijos mokslo krypties taryboje:

Pirmininkas:

Prof. habil. dr. Aivaras Kareiva (Vilniaus universitetas, fiziniai mokslai, chemija – 03P).

Nariai:

Prof. habil. dr. Albertas Malinauskas (Fizinių ir technologijos mokslų centras, fiziniai mokslai, chemija – 03 P)

Prof. habil. dr. Audrius Padarauskas (Vilniaus universitetas, fiziniai mokslai, chemija – 03P)

Doc. dr. Ingrida Ancutienė (Kauno technologijos universitetas, fiziniai mokslai, chemija – 03 P)

Doc. dr. Jūratė Senvaitienė (P. Gudyno restauravimo centras, fiziniai mokslai, chemija – 03P)

Official Opponents:

Doc. dr. Audronė Gefenienė (Lietuvos edukologijos universitetas, fiziniai mokslai, chemija – 03P)

Dr. Loreta Tamašauskaitė-Tamašiūnaitė (Fizinių ir technologijos mokslų centras, fiziniai mokslai, chemija – 03 P)

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Adresas: Goštauto 9, LT-2600 Vilnius, Lietuva

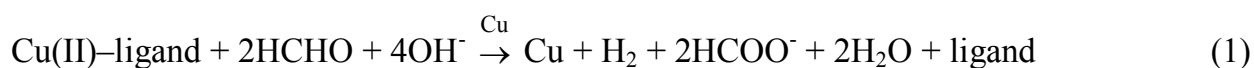
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INTRODUCTION

Electroless metal coating technique is one of the elegant ways of metal coating by controlling the temperature and pH of the plating bath in which there is no usage of electric current. The industrial electroless copper plating solution containing formaldehyde as reducing agent are known from the middle of the last century and are widespread in the practice up to now. Electroless copper coatings are being used on plastics, ceramics, polymers and other non-conductive materials. However many chemical compounds used in such kind technological processes are hazardous for total environment, therefore the efforts are made to displace those substances with less hazardous or purely harmless compounds.

Generally the total autocatalytic process of electroless copper deposition is described by following equation:



Ethylenediaminetetraacetic acid (EDTA) is the most widely used ligand in alkaline electroless copper plating baths due to its perfect chelating properties. From the other hand these excellent complexing properties of EDTA create environmental hazards because of the binding of heavy metal ions into soluble, very stable and hardly decomposable complexes in a wide pH range. In addition, EDTA is very weakly biodegradable. Therefore the efforts are made to displace mentioned copper(II) ligand with less hazardous or purely harmless compounds. Such kind attempts are documented when replacing EDTA with other ligands in alkaline electroless copper plating systems. Generally two classes of chemical compounds were proposed as EDTA alternative, namely alditols (polyhydroxylic alcohols) and hydroxypolycarboxylic acids.

Therefore the aim of the work presented herein was a comparatively study of the process of electroless copper deposition from alkaline formaldehyde-containing solutions, using citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) and different isomers of tartaric acid (2,3-dihydroxybutanedioic acid), namely L- and D-tartrate, and their racemic mixture DL-tartrate at different pH values and temperatures.

The aim of the work was to investigate peculiarities of formaldehyde containing alkaline electroless copper deposition systems using environment friendly hydroxycarboxylic acids as Cu(II) ligands.

The main tasks of the work were as follows:

1. To investigate or define more precisely equilibria in alkaline formaldehyde containing electroless copper solutions using citric acid and D-, L- and DL-isomers of tartaric acid as Cu(II) ligands.
2. To estimate the stability of electroless copper deposition solutions, to investigate influence of pH and concentration of ligand on the rate of electroless copper reduction and characteristics of coatings deposited using citric acid as Cu(II) ligand.
3. To investigate influence of temperature, pH and the nature of ligand on the rate of electroless copper reduction and characteristics of coatings deposited using isomers of D-, L- and DL-tartaric acid as Cu(II) ligand.
4. To perform the measurements of the real surface area of electrochemically and electrolessly deposited copper coatings.
5. To investigate the parameters of anodic oxidation of formaldehyde on electrolessly deposited copper coatings obtained from solutions containing D-, L- and DL-tartrate as Cu(II) ligand.

Scientific novelty and practical value of the work

Two new Cu(II) ligands, namely citric acid and D-isomer of tartaric acid, were applied for the systems of electroless copper deposition. The results of the investigations show that the ligands mentioned can be successful applied in the processes of electroless copper deposition using formaldehyde as reducing agent.

The equilibria of Cu(II) ions was defined more precisely in alkaline solutions of citric acid and D-, L- and DL-isomers of tartaric acid.

The peculiarities of the process of autocatalytic reduction of Cu(II) from solutions containing citric acid D-, L- and DL-tartrate as Cu(II) ligands was investigated in details, the characteristics of electrolessly deposited coatings were estimated.

Concerning environmental aspects of the use hydroxycarboxylic acids, it is worth to noting that copper recovery from used electroless copper plating solutions containing

citric acid and D-, L- and DL-tartrates as Cu(II) ligands is much less complicated than for solutions using conventional ligands such as EDTA or Quadrol, since the Cu(II) complexes with citrate and tartrate can be precipitated and decomposed by simply lowering the solution pH up to acidic conditions (with some technological peculiarities). The remaining hydroxycarboxylic acids are environmentally benign, i. e. it do not form stable complexes with heavy metals under natural conditions and there are easily biodegraded.

Approbation of the dissertation. Two publications have been published in the scientific journals on the theme of dissertation. The research results have been presented at 3 Lithuanian national scientific conferences.

1. EXPERIMENTAL

1.1. Chemicals and solutions

Analytical grade reagents were used, and the formaldehyde source was formalin (37 % HCHO) solution. Formaldehyde concentration in the stock solution was determinate iodometrically. Measurements of pH and pH-metric titrations were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode.

1.2. Spectrophotometric measurements

The visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrometer at $20 \pm 1^\circ\text{C}$ in 1.0 cm path length quartz cells. The optical blank solution was pure water.

1.3. Copper surface formation

The substrate was a smooth Pt sheet (1×1 cm) electroplated with Cu for 20 min from acid copper solution ($1.0 \text{ mol l}^{-1} \text{ CuSO}_4 + 0.5 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$) at 1.5 A dm^{-2} . Before the electroless plating the electroplated substrate was activated for 30 s in acid PdCl_2 solution (1 g l^{-1}). The main electroless copper plating experiments were carried out for 30 or 60 min at $10\text{-}30^\circ\text{C}$ in 50 ml of the solution containing (mol l^{-1}): $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – 0.05; ligand – from 0.10 to 0.30; formaldehyde – 0.15; NaOH – up to pH needed. The

amount of copper deposited was determined by mass difference. All measurements were repeated at least three times and mean value calculated.

1.4. Determination of the real surface area of the Cu coatings obtained

The copper surface determination method is based on the underpotential deposition of the thallium monolayer on the Cu electrode surface. The measurements were carried out at 25°C in 1 M Na₂SO₄ solution containing 1 mmol l⁻¹ TlNO₃. Before the measurements copper oxides were removed from the surface: the working Cu electrode was kept at -0.80 V for 5 s. Then the electrode was kept at +0.15 V for 5 s (for dissolving the bulk Tl deposit). A Tl monolayer was formed at -0.49 V for 200 s. Then the Tl monolayer was dissolved using anodic scanning of the potential up to -0.1 V (scanning rate 50 mV s⁻¹). By integration of the potentiodynamic curve obtained (in the range from -0.39 to -0.10 V), the quantity of electricity (Q , μC) used for anodic dissolution of the Tl monolayer was calculated.

The real surface area (in nano-scale dimensions) of the Cu electrode (S_R , cm²) was calculated using the Tl monolayer capacity Q_{Tl} (the quantity of electricity necessary to form a monolayer on 1 cm² of electrode) equal in this case to 112 μC cm⁻² :

$$S_R = Q/Q_{Tl} \quad (2)$$

The surface nano-scale roughness factor R_f is calculated as a ratio of real and geometric surface areas:

$$R_f = S_R/S_G \quad (3)$$

1.5. Voltammetric measurements

Voltammetric curves were obtained by standard electrochemical equipment (potentiostat PI-50, sweep generator PR-8, xy-recorder H-307, thermostatted electrochemical cell JES-1 (Belarus) and thermostat UH-4 (Germany). The solutions were deaerated by Ar. The auxiliary electrode was Pt foil, and the reference electrode was Ag/AgCl with a saturated KCl solution.

The solutions were thermostated at 20 °C in 0.1 mol l⁻¹ Na₂SO₄ supporting electrolyte, the Cu electrode was potentiostated at -0.9 V and then voltammograms were recorded in the potential range -0.9 to + 0.1 V (SHE), potential scanning rate being 5 mV s⁻¹. All potentials are presented in reference to standard hydrogen electrode (SHE).

Mixed potential of copper electrode (E_{mix}) during the process of electroless copper deposition (the open circuit potential) was measured by means of xy-recorder H-307 (Russia)

using the Ag/AgCl reference electrode with a saturated KCl solution. All potentials are presented in reference to SHE.

1.6. Electrochemical quartz crystal microbalance (EQCM) measurements

AT-cut quartz crystals of 6 MHz fundamental frequency (from Intelemetrics Ltd., UK) sputtered by gold from both sides were used. They were connected to a home-built oscillator. Their electrochemically and piezoelectrically active geometric areas were 0.636 and 0.283 cm², respectively. Quartz crystals were installed at the bottom of the cell of working volume ca. 2 ml. The upper part of the cell contained the Pt-wire counter electrode, joints for the electrolyte inlet and the Luggin capillaries, and the electrolyte outlet tube. The construction of the cell allowed exchange of the solution under controlled electrode potential. The electrolytes in the supply bottles were constantly purged with Ar. Prior to the experiments a copper layer was electrodeposited onto a gold sublayer on quartz crystal mounted in the cell from a solution containing 1.0 mol l⁻¹ CuSO₄ and 0.5 mol l⁻¹ H₂SO₄ at a current density of 10 mA cm⁻² for 15-20 s.

EQCM measurements were carried out using a precision frequency counter Ch3-64 and two digital voltmeters B7-46 connected to a PC through an IEEE 488 interface (all the equipment was made in Russia). A programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia) were used to control the electrode potential. The potential was measured with respect to an Ag/AgCl/KCl_{sat} reference electrode and is given below vs. a standard hydrogen electrode (SHE). The electrode potential, the faradaic current and the frequency measured (counted with an accuracy of 0.01 Hz) were transferred to the PC every 1.3 s. A calibration constant 33.5 Hz s⁻¹ per 1 mA was found in EQCM measurements of copper deposition from alkaline Cu(II) solutions containing trisodium citrate as ligand.

2. RESULTS AND DISCUSSION

2.1. Equilibria in alkaline Cu(II)-citrate solutions

The titration curves of solutions containing equimolar quantities of trisodium citrate and Cu(II) salt as well as containing fivefold excess of trisodium citrate showed an inflection after addition of ca. one equivalent of base per mole of copper(II) salt (Fig. 1). This confirms that in the case of Cu(II) complex formation with trianion of citric acid

at pH's higher than 6-8, the dissociation of the proton from hydroxyl group takes place and Cu(II) ions additionally combine with citrate trianion through deprotonated OH-group. The stoichiometry of the Cu(II) complex formed is 1:1, since the light absorbance does not depend on ligand concentration beginning from the metal-to-ligand ratio equal to 1:1. Taking into account, that finally Cu(II) is combined with tetraanion of citric acid (see above), the composition of the complex formed at pH = 12 is CuCit^{2-} .

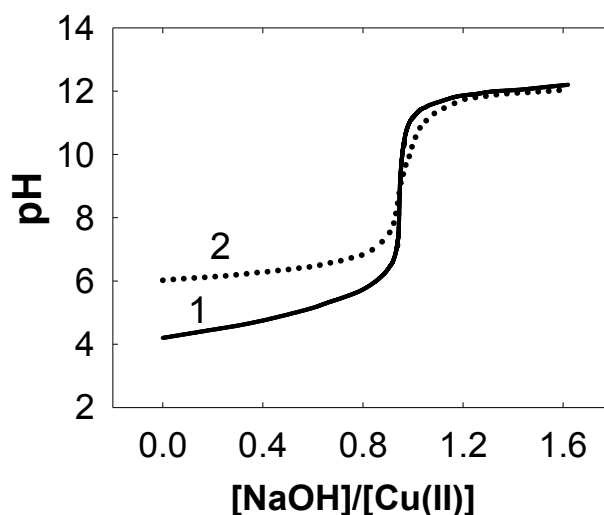


Fig. 1. Titrations curves of solutions of copper(II) sulphate and trisodium citrate with 1 mol l⁻¹ sodium hydroxide. Initial concentrations (mol l⁻¹): [Cu(II)] – 0.05, [Na₃Cit]: 1) – 0.05 and 2) – 0.25.

2.2. Electroless copper deposition from solutions containing citrate as Cu(II) ion ligand

In solutions with an excess of trisodium citrate, autocatalytic reduction of Cu(II) by formaldehyde starts at pH 12 (Fig. 2). The plating rate near the lower pH limit (pH 12) is ca. 0.5 $\mu\text{m h}^{-1}$. With further increase in solution pH, the plating rate rises sharply reaching maximum values at a pH near 12.75 (Fig. 2), and then decreases sharply as the pH is further elevated (Table). The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 3 μm (Fig. 2). It is worth to note that the plating rate practically does not depend on excess of ligand, i. e. the plating rate remains constant even if sixfold excess of trisodium citrate is used, comparing with twofold starting-excess (Fig. 3). It should be emphasized that the plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed at least during one hour.

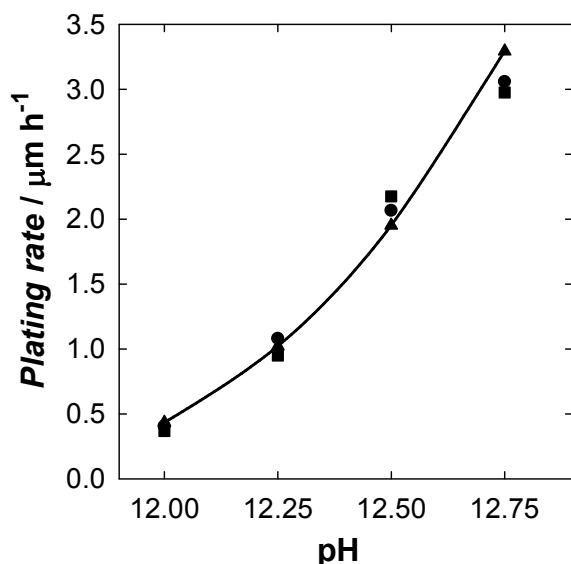


Fig. 2. Dependence copper plating rate on pH. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{Na}_3\text{Cit}]$: (●) – 0.1, (▲) – 0.2, (■) – 0.3.

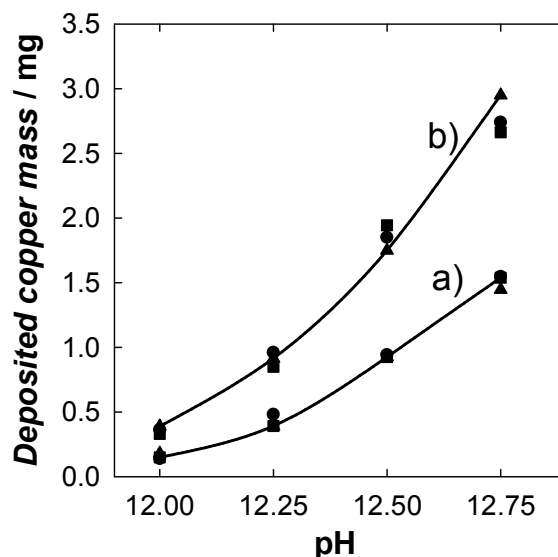


Fig. 3. Dependence of electrolessly deposited copper mass on pH. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{Na}_3\text{Cit}]$: (●) – 0.1, (▲) – 0.2, (■) – 0.3. Plating time: a) – 0.5 hour, b) – 1 hour.

Dependencies of copper deposit mass on electroless copper plating solution pH obtained in 0.5 and 1 hour (Fig. 3, curve a) and curve b), respectively) have the same exponential shape. At the same pH values the mass of copper deposited in 1 hour is practically two times higher than that obtained in 0.5 hour. It can be predicted from results obtained that process of electroless copper deposition starts without longer induction period and quasi-stationary plating conditions are reached after relatively short time at pH values investigated (i. e. pH 12-12.75). The measurements of mixed potential (E_{mix}), i. e. potential of copper electrode under open circuit conditions, during electroless copper deposition process confirm above-mentioned assumption (Fig. 4). During the initial period (i. e. in the first 1-2 minutes) E_{mix} reaches its most negative value, later shifting to more positive potentials and after ca. 15 minutes it remains practically constant (or shifts negligible to more positive potentials) due to the establishment of quasi-stationary plating conditions. After establishing of quasi-stationary conditions the mixed potential shifts continuously to more negative values with the rise in solution pH (Fig. 4).

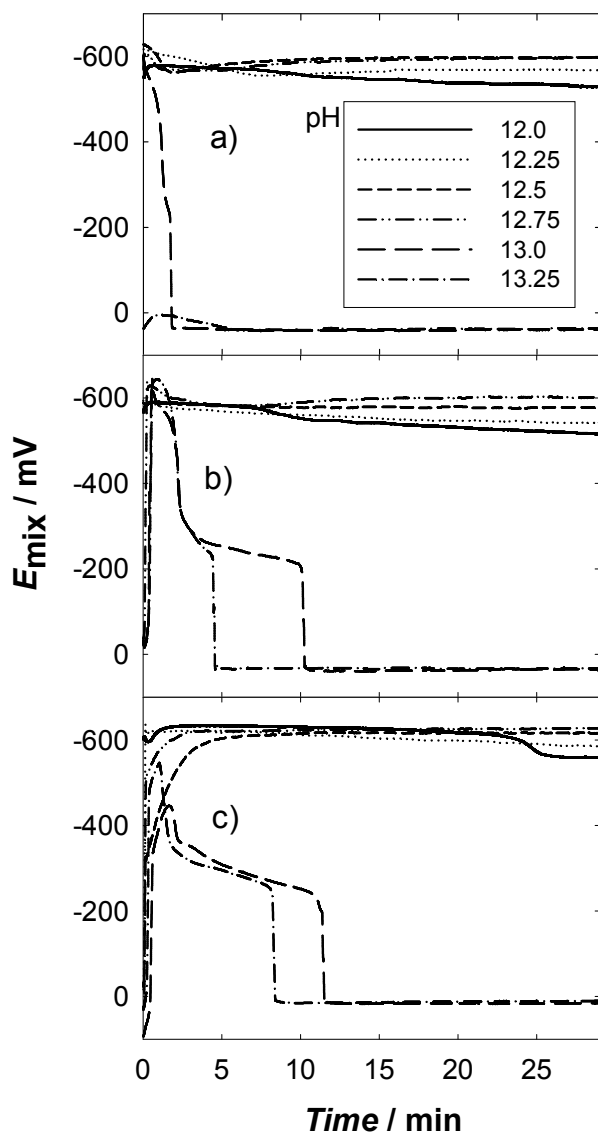


Fig. 4. Time dependence of mixed potential (E_{mix}) of copper electrode during electroless copper plating. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{Na}_3\text{Cit}]$: a) $- 0.10$, b) $- 0.20$, c) $- 0.30$.

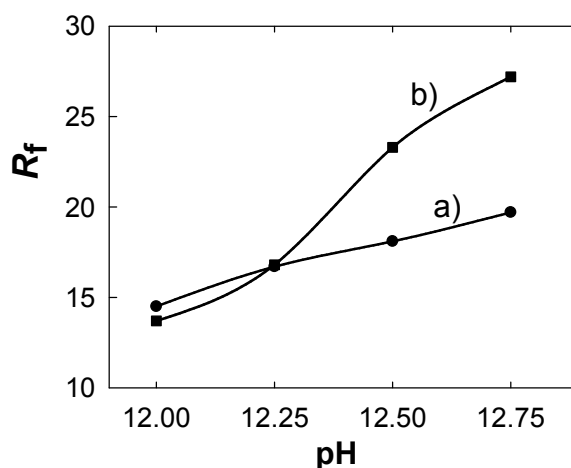


Fig. 5. Dependence copper surface roughness factor of electrolessly deposited copper coatings on pH. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{Na}_3\text{Cit}]$: a) $- 0.1$, b) $- 0.2$. Plating time 1 hour.

From Cu(II) -citrate solutions copper coatings deposited by the electroless technique have more developed surfaces than that of electroplated copper ($R_f = 1.5$) and R_f values that vary widely, from ca. 14 up to 28 (Fig. 5). If one observes the pH-dependence in the R_f of the copper deposits, the interrelationship among R_f and copper plating rates is evident (cf. Figs. 2 and 5). The trend being more expressed for solutions with higher excess of trisodium citrate (Fig. 5, curve b). This correlation could

correspond to the known general trend for e. g. electroplating, that formation of smoother metal deposits occurs at lower deposition rates.

A particular discussion is needed concerning data obtained on electroless copper plating at higher pH values, namely at pH 13.0-13.25, where a dramatically decrease in process rate was observed (cf. Fig. 4 and Table). The decrease in plating rate could be caused by changes in the catalytic surface state and characteristics of the Cu surface obtained at higher pH values may be important. For example the surface may be less catalytically active due to the formation of Cu(I) species. The fact of Cu surface passivation at higher pH's, i. e. formation of Cu_2O , confirm measurements of E_{mix} , showing that at pH 13.0-13.25 the values of E_{mix} become relatively very positive and reach a constant value equal to ca. from 0 to +20 mV (Fig. 4).

Table. Dependence of increment of copper electrode mass (Δm) after immersion in solution for electroless copper plating on time and pH. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCH}] - 0.15$, and excess of trisodium citrate $[\text{Na}_3\text{Cit}]$ is itemized in Table captions.

pH	$[\text{Cu(II)}]/[\text{Na}_3\text{Cit}] = 1:2$		$[\text{Cu(II)}]/[\text{Na}_3\text{Cit}] = 1:4$		$[\text{Cu(II)}]/[\text{Na}_3\text{Cit}] = 1:6$	
	Δm (mg) after 0.5 h	Δm (mg) after 1 h	Δm (mg) after 0.5 h	Δm (mg) after 1 h	Δm (mg) after 0.5 h	Δm (mg) after 1 h
13.00	0.25	0.35	0.90	1.10	0.80	1.00
13.25	0.20	0.30	0.60	0.85	0.70	0.80

In solutions containing twofold excess of citrate the passivation of copper electrode occurs practically immediately after immersion of electrode in solution, when solution pH value is the highest, i. e. 13.25, whereas at pH = 13.0 the copper plating process starts (potential of electrode becomes negative like at lower pH's where electroless copper deposition was observed), but in couple minutes it stops. The E_{mix} shifts continually (with short stop at ca. -250 mV) to more positive potentials and reaches a constant value at ca. +20 mV after around 2-2.5 minutes, and later the value of E_{mix} remains constant (Fig. 4 a). It is interesting that we have observed the increase in electrode mass after its exposure in solution for 0.5 as well as 1 hour. The mass

increment is quite moderate and is in the range from 0.2 to 0.35 mg (Table). It is clear that the mass increment can not be connected with deposition of metallic copper at potential values mentioned and can be accounted for the formation of Cu_2O film.

Quite unexpected results were obtained when using higher (fourfold or sixfold) excess of citrate. The increase in electrode mass is much higher comparing with that obtained in solutions with twofold excess of citrate and could reach 1.1 mg per hour (Table). Comparison of time dependencies of E_{mix} in solutions with various concentrations of citrate (Fig. 4) shows that additional process occurs after ca 2-3 min. after immersion of copper electrode in solution – the shift of E_{mix} stops at ca. -300 mV. The duration of this stop depends on solution pH and concentration of citrate, being longer at higher pH's and citrate concentrations and reaching maximum ca. 10 min (Figs. 4 b and 4 c). Later E_{mix} shifts sharply to most positive potentials and remains constant (Figs. 4 b and 4 c).

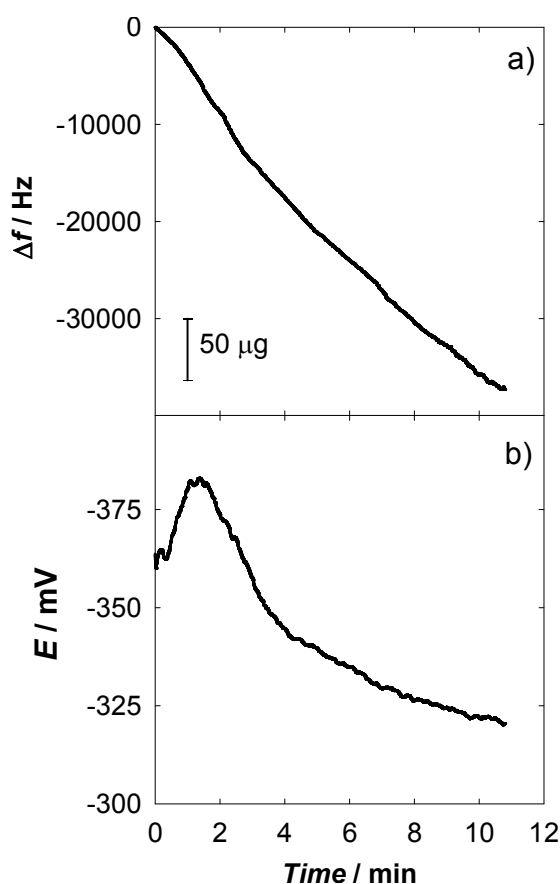


Fig. 6. The change in quartz crystal frequency (a) and mixed potential (E_{mix}) of copper electrode (b) during electroless copper sputing. The solution contained (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{Na}_3\text{Cit}] - 0.2$; pH – 13.0.

Fig. 6 represents time dependent decrease in quartz crystal frequency (corresponding to mass increase) and simultaneously measured values of E_{mix} . Conversion of the decrease in quartz crystal frequency during ca. 11 minutes (Fig. 6 a) gives the mass increase equal to 0.3 mg. The active surface area of electrode used in EQCM measurements is ca. three times lower than that used in ordinary experiments, therefore the recalculated mass for electrode with surface area of 2 cm² would be ca. 0.9 mg. When comparing this value with the data of Table it is seen that the main increase in electrode mass is obtained at ca. -300 mV, i. e. during initial period.

2.3. Equilibria in alkaline Cu(II)-tartrate solutions

The light absorbance spectra of Cu(II) with several tartrate isomers show that their optical characteristics are different. The light absorbance spectra of Cu(II) in alkaline solutions of individual D- and L- tartrate isomers practically coincide. Spectrum of Cu(II) complex with DL-tartrate is quite different from that of Cu(II) with L- and D-tartrate. The differences could be explained by different steric structure of the complexes formed. It can be noted that the light absorbance spectra of Cu(II) complex with DL-tartrate coincide with equimolar mixture of D- and L-tartrate. (Fig. 7).

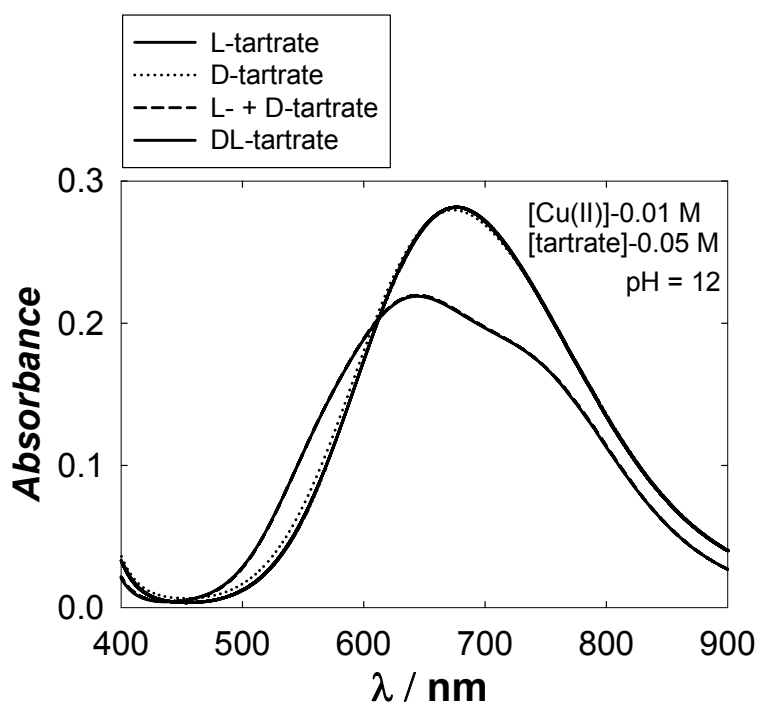


Fig. 7. Light absorbance spectra of Cu(II) in alkaline solutions of L-, D-, and DL-tartrate

2.4. Electroless copper deposition from solutions containing tartrate as Cu(II) ion ligand

In solutions containing an excess of the ligand (L-, D- or DL-tartrate) the autocatalytic reduction of Cu(II) by formaldehyde was investigated in pH region from 12 to 13. It is worth to noting, that from the data of Fig. 8 can be concluded, that no surface passivation processes are observed in the systems under investigation: the comparison of the thickness of copper coating obtained after 30 min, which was recalculated to values corresponding to that after 1 hour, i. e. multiplied by two (the plating rate dimension being $\mu\text{m h}^{-1}$) (Fig. 8; 1 a), 1 b) and 1 c)), with that obtained after 1 hour plating (Fig. 8; 2 a), 2 b) and 2 c)) are very close to each other, showing no tactile retardation process.

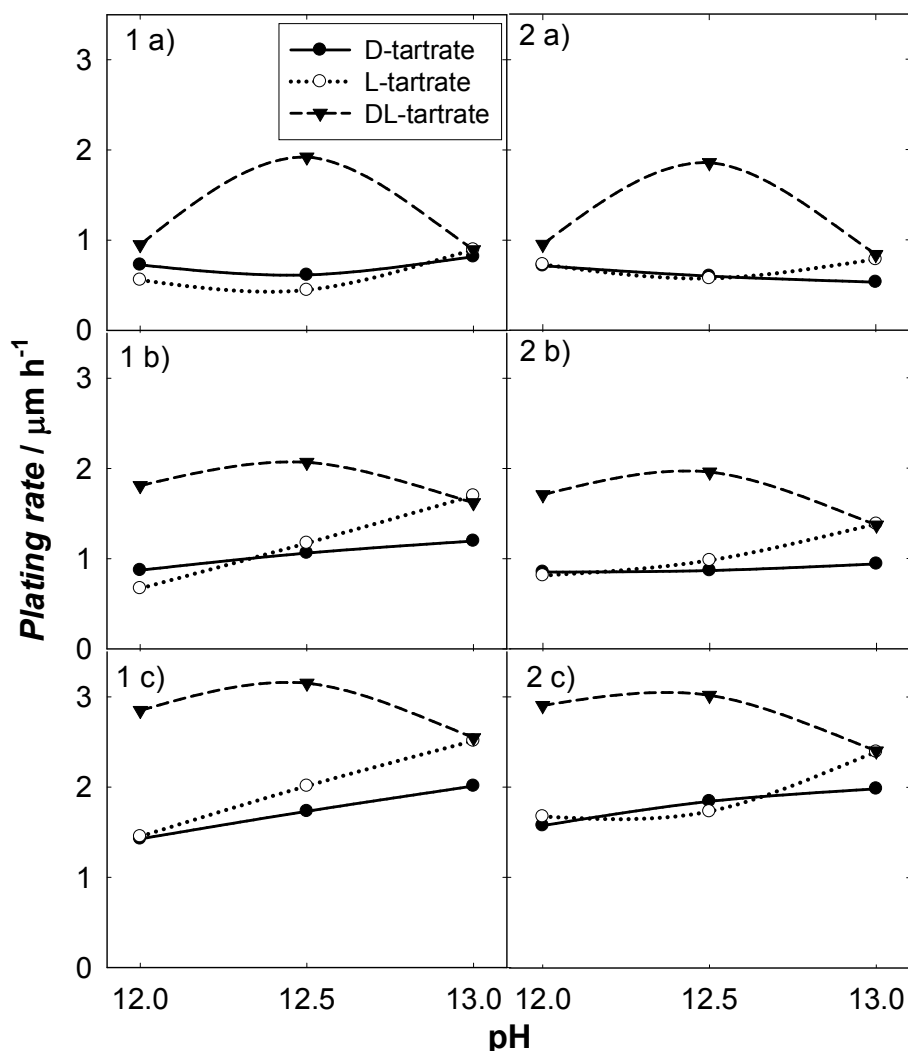


Fig. 8. Dependence of copper plating rate on pH and ligand. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{tartrate}] - 0.15$. Temperature a) $- 10^\circ\text{C}$, b) $- 20^\circ\text{C}$, c) $- 30^\circ\text{C}$. Plating time: 1 - 0.5 h, 2 - 1 h.

The data of the measurements of mixed potential confirm this conclusion (see below). In solutions with the lowest plating temperature (10°C) and lowest and highest investigated pH values (pH 12 and pH 13) the plating rates obtained are very close for all used isomers of tartaric acid (Fig. 8, 1 a) and 2 a)) and do not exceed 1 $\mu\text{m h}^{-1}$. The comparable rates are observed for D-and L-tartrate also at pH 12.5, whereas in the case of the racemic mixture of DL-tartrate, the sharp increase in plating rate is visible at pH 12.5 reaching ca. 2 $\mu\text{m h}^{-1}$. Rather similar trends are observed when electrolessly depositing copper at higher temperatures (20 and 30°C), except values obtained for L- and D-tartrate at pH 13, where copper plating rate from L-tartrate containing solutions is apparently higher than that from D-tartrate containing solutions. The highest plating rate – ca. 3 $\mu\text{m h}^{-1}$ – was obtained from the solutions containing the racemic mixture of DL-tartrate at pH 12.5 (Fig. 8 1 c) and 2 c)).

The clear correlation between plating rate and values of E_{mix} (Fig. 9) is observed – the highest plating rates under the similar conditions were determined in DL-tartrate containing solutions (Fig. 8), which exhibit the most positive E_{mix} values (Fig. 9), whereas the lowest plating rates were estimated in D-tartrate containing solutions. The highest numerical value of the electroless copper deposition rate obtained – 3.2 $\mu\text{m h}^{-1}$ – was achieved in DL-tartrate solutions with pH = 12.5 at 30°C, the E_{mix} numerical value being -321 mV, i. e. corresponding to one of the most positive values measured (Fig. 8, 9). In opposite, the lowest numerical value of the electroless copper deposition rate obtained – 0.4 $\mu\text{m h}^{-1}$ – was measured in L-tartrate solutions with pH = 12.5 at 10°C, the E_{mix} numerical value being -456 mV, i. e. corresponding to the most negative value measured in our experiments (Fig. 8, 9).

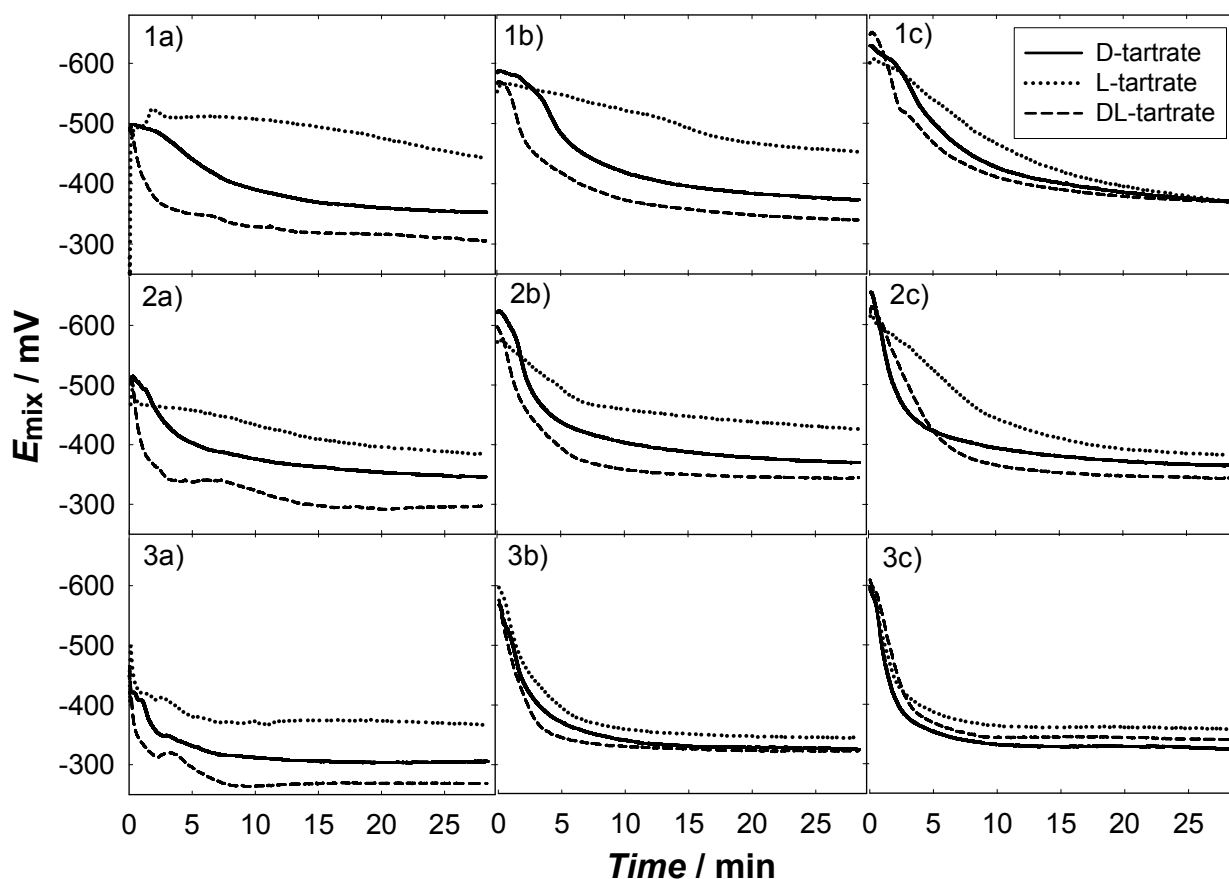


Fig. 9. Time dependence of mixed potential (E_{mix}) of copper electrode during electroless copper plating. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{tartrate}] - 0.15$. Copper deposition temperature: 1) 10°C , 2) 20°C , 3) 30°C ; pH: a) 12.0, b) 12.5, c) 13.0.

From Cu(II) -tartrates solutions electrolessly deposited copper coatings in all cases have more developed surface, then that of electroplated copper ($R_f = 1.5$), and the roughness factor varies in a wide range of values – from 1.6 to 12.2 depending on electroless copper plating solution pH, ligand used and temperature (Fig. 10).

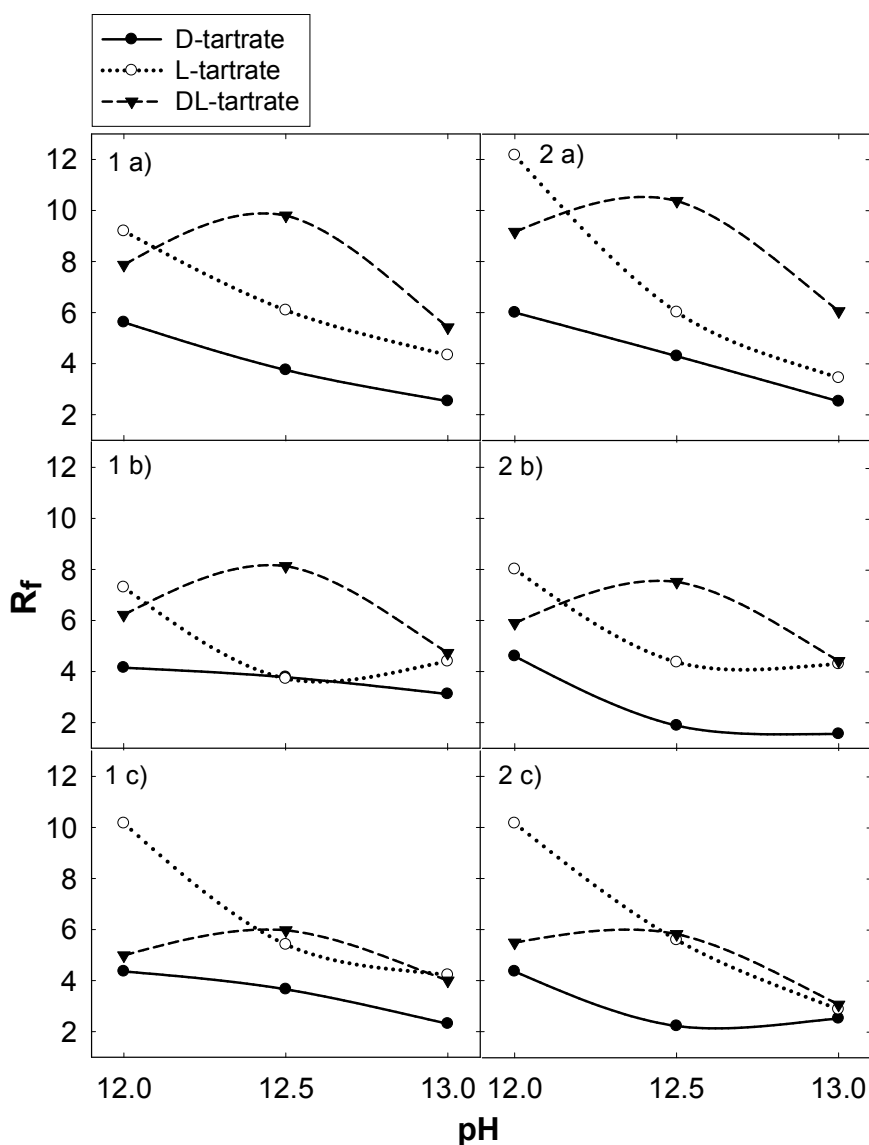


Fig. 10. Dependence of the copper surface roughness factor of electrolessly deposited copper coatings on pH and nature of ligand. Solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{tartrate}] - 0.15$; temperature: a) 10°C , b) 20°C , c) 30°C . Plating time 1 - 0.5 h, 2 - 1 h.

It can be noted, that in general the roughness of the coatings obtained after 0.5 hour is rather analogous to that obtained after 1 hour (Fig. 10). The results presented are in good agreement with the data of the measurements of the mixed potential of copper electrode during the process of electroless copper plating (see above) – commonly the values of the mixed potential reach approximately constant values after ca. 15-20 min from the beginning of the process of electroless plating, and later plating occurs under the quasi-stationary conditions, the probability of substantial changes in the real surface area of the electrode being low.

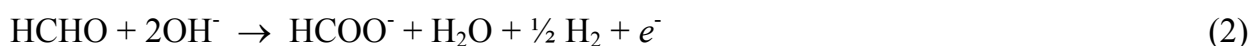
Generally, the rise in temperature results smoother coatings, i. e. with the surfaces of lower roughness factor (R_f) (Fig. 10).

pH- R_f dependencies for each used ligand differ. When using DL-tartrate as Cu(II) ion ligand, the shape of pH- R_f dependence (Fig. 10) remind that of pH-plating rate (Fig. 8), i. e. with distinct maximum at pH 12.5. In the case of L- or D-tartrate the shape pH- R_f dependence (Fig. 10) is opposite than that of pH-plating rate dependence – the highest values of R_f are observed at lower pH limit investigated, and the increase in solution pH results decrease in R_f . In all cases at the same solution pH and different used ligand the smoothest coatings were observed when using D-tartrate as Cu(II) ligand.

The smoothest copper coating was deposited from D-tartrate solutions at pH 13 (20°C) – the $R_f = 1.6$ was very close to that of electroplated copper ($R_f = 1.5$). The highest R_f values were obtained for copper coatings deposited from L-tartrate solution at pH 12 and 10°C ($R_f = 12.2$), and from DL-tartrate solution at pH 12.5 and the same temperature ($R_f = 10.4$).

2.5. Voltammograms of copper electrode in alkaline solutions of formaldehyde and formaldehyde oxidation rates

Voltammograms were recorded using four different types of copper electrodes. The surface of the first electrode was formed by electroplating from an acidic copper(II) sulphate electrolyte. The other three types were prepared by an electroless copper plating technique (at 10, 20 and 30°C) from solutions containing D-tartrate, L-tartrate and DL-tartrate, respectively, as Cu(II) ligand at pH values corresponding to those of the solutions under electrochemical investigations. Figure 11 presents voltammograms of electroplated copper electrode in alkaline solutions of formaldehyde. At the positive-going potential scan anodic current is observed over the potential interval *ca.* 0.6 V; this current is known to be a result of anodic formaldehyde oxidation according to the equation (2), since in the absence of formaldehyde no current is observed in this potential region:



It is seen, formaldehyde anodic oxidation current dependence on pH and increases with rise of solution pH from 12 to 13 (Fig. 11).

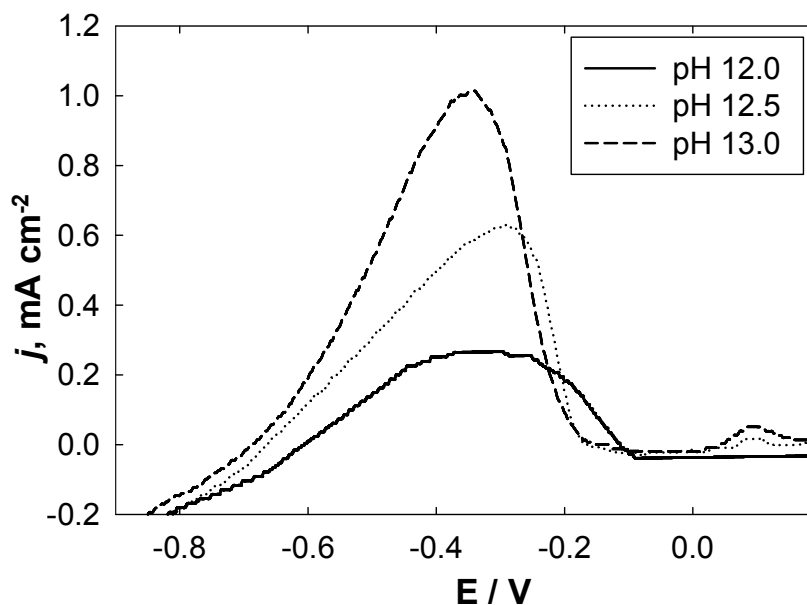


Fig. 11. Voltammograms of copper electrode (formed by electroplating) in alkaline solutions of formaldehyde. Solution composition (mol l^{-1}): $[\text{Na}_2\text{SO}_4] - 0.1$; $[\text{HCHO}] - 0.15$. Solution temperature – 20°C .

The shape and the values of the formaldehyde anodic oxidation current differ significantly, when comparing such kind data obtained on electroplated copper electrode with that measured on electrolessly deposited copper coatings (cf. Fig. 11 and Fig. 12). In general case the values of the anodic oxidation of formaldehyde on electrolessly deposited copper surfaces are much higher (in some cases more than five times) than that obtained on electroplated copper electrode (cf. Figs. 11 and 12).

When analyzing the data of Figure 12, no large differences are observed in anodic oxidation curves of formaldehyde at pH 12.0, i. e. all copper coatings electrolessly deposited from solutions containing D-, L- and DL-tartrate as Cu(II) ligands at 10, 20 and 30°C exhibit similar properties, the lowest value obtained for L-tartrate (plating at 30°C), and the highest – for DL-tartrate (plating at 30°C). In all cases in solutions with higher pH value and equal to 12.5, the currents have 3-4 times higher values, than those obtained at pH = 12.0 (Fig. 12). At pH = 12.5 the highest formaldehyde anodic oxidation peak current values were measured on copper electrodes coated with electroless copper at 20°C in solutions of all three isomers. When comparing the copper coatings deposited from solutions of different isomers at the same temperature (10, 20 or 30°C), it can be

noted, that the currents of formaldehyde anodic oxidation (at pH 12.5) mainly are highest in the case of DL-tartrate, and lowest for D-tartrate (Fig. 12). The same general trend is evident during the oxidation of formaldehyde at pH 13 (Fig. 12). An additional interesting and clear seen peculiarity was unrolled at the mentioned pH value – for all three above mentioned kinds of electrolessly deposited copper coatings the highest formaldehyde oxidation rates were obtained for coatings, deposited at the lowest, i. e. 10° C, temperature, whereas the coatings deposited at 30°C are at the least active in anodic oxidation of formaldehyde (Fig. 12).

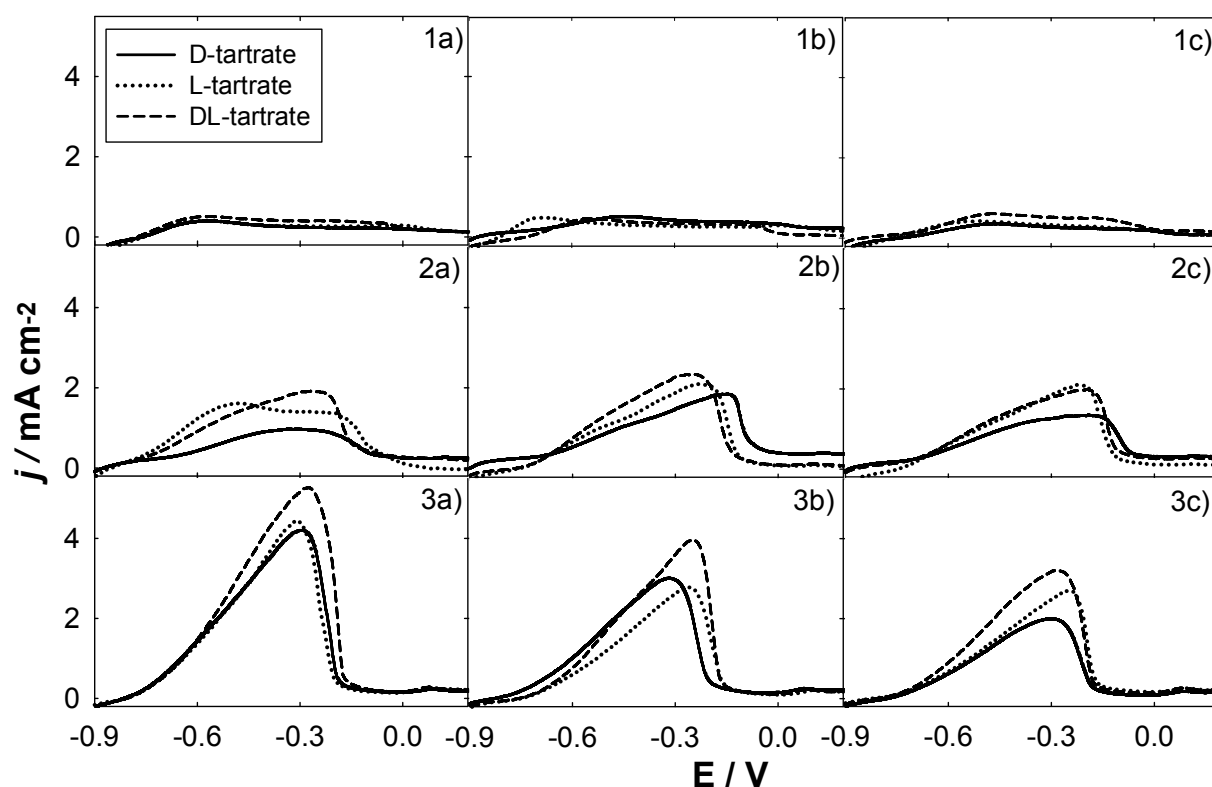


Fig. 12. Voltammograms of copper electrode in alkaline solutions of formaldehyde. Solution composition (mol l^{-1}): $[\text{Na}_2\text{SO}_4] - 0.1$; $[\text{HCHO}] - 0.15$. Solution temperature – 20 °C. Electrode surface was formed by electroless plating from tartrate isomers containing solutions. Plating solution composition (mol l^{-1}): $[\text{Cu(II)}] - 0.05$, $[\text{HCHO}] - 0.15$, $[\text{tartrate}] - 0.15$. Plating conditions: pH – 1) 12.0, 2) 12.5, 3) 13.0; temperature – a) 10°C, b) 20°C, c) 30°C.

The specific activity of copper surface (formaldehyde anodic oxidation peak current per unit of real surface area) was calculated from the data in Figure 12 for comparing the electrocatalytic properties of various copper layers obtained by electroless plating technique using different isomers of tartaric acid as Cu(II) ligands. The data presented in Fig. 13 compare the pH dependencies of HCHO anodic oxidation current

peak density (corresponding to the geometrical surface area) (a), HCHO anodic oxidation current peak density (corresponding to the real surface area) (b) on electrolessly deposited coatings from solutions of D-, L- and DL-tartrate as copper(II) ligand at 20°C. Very similar tendency is observed when comparing results of investigations carried out at 10 and 30°C, with those conducted at 20°C. It can be noted that the trends are practically the same for D-tartrate, L-tartrate and DL-tartrate containing solutions, the differences are only in numerical values of parameters. It can be noted that in all investigated cases the shape of formaldehyde anodic oxidation peak current dependence on solution pH for currents obtained for the geometrical surface area is very similar to that calculated for the real surface area (Fig. 13). The activity of coatings decrease with increasing of temperature of electroless plating solution.

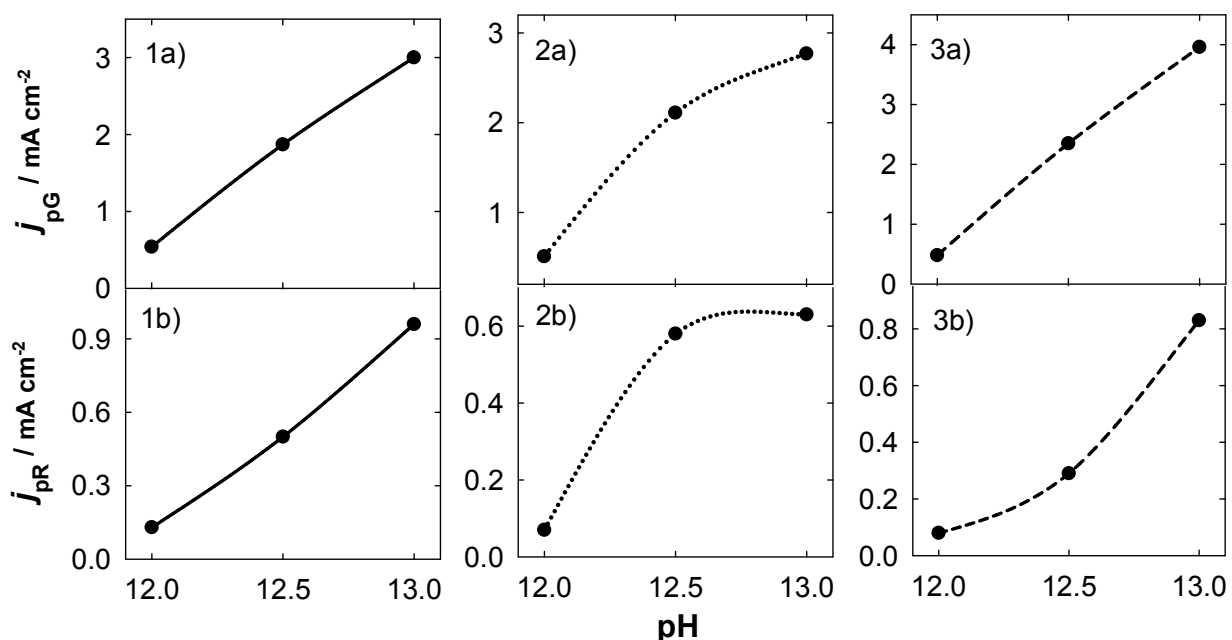


Fig. 13. Dependence of HCHO anodic oxidation current peak density (corresponding to the geometrical surface area) (a) and HCHO anodic oxidation current peak density (corresponding to the real surface area) (b) on pH. Solution composition (mol l^{-1}): [Cu(II)]-0.05, [HCHO]-0.15, [tartrate]-0.15: 1) D-tartrate, 2) L-tartrate, 3) DL-tartrate. Temperature of solutions – 20°C.

3. CONCLUSIONS

1. When investigating Cu(II) complex formation with citrate and D-, L- and DL-tartrate in alkaline solutions by means of pH-metric titration and spectrophotometry, it was found that Cu(II) ions promote deprotonation of the –OH groups of citric and tartaric acids, forming stable complexes with the mentioned ligands.
2. The possibility of using of citric acid as Cu(II) ligand in electroless copper plating systems is shown: the autocatalytic reduction of Cu(II) by formaldehyde from solutions containing trisodium citrate as the ligand begins at pH above 12, accelerates with a further increase in pH, reaches a maximum value at pH 12.75 (ca. 3 $\mu\text{m/h}$ at 20 °C), then slows down at higher pH values.
3. The real surface area of copper coatings electrolessly deposited from trisodium citrate-containing solutions depends on solution pH and rises with increase in solution alkalinity. The roughness factor (R_f) of copper coatings obtained could reach 28.
4. The possibility of using of all investigated isomers of tartaric acid, namely D-tartrate, L-tartrate and and racemic mixture of DL-tartrate, as Cu(II) ligands in electroless copper plating systems is shown. The autocatalytic reduction of Cu(II) by formaldehyde from solutions containing mentioned ligands begins at pH about 12.
5. Under equal conditions at pH 12.0 – 13.0 the kinetics of electroless copper deposition from solutions containing D-, L- and DL-tartrate as Cu(II) ligands depends: a) on nature of the ligand – the lowest rates were observed for D-tartrate, whereas the highest – for DL-tartrate; b) on solution pH – the maximum deposition rate was found at solution pH 13.0 for D- and L-tartrate, whereas in the case of DL tartrate the maximum rate was achieved at pH 12.5; c) on temperature – in the case of all used isomers of tartaric acid the electroless copper deposition rate increased with the increment of temperature.
6. The mixed potential of copper electrode (E_{mix}) in solutions for electroless copper deposition depends on the nature of the ligand used. Using trisodium citrate relatively negative E_{mix} values were measured (ca. -520 – -630 mV), whereas in the case of tartrate isomers comparatively more positive values were observed (ca. -300 – -430 mV).

7. The real surface area of copper coatings electrolessly deposited from tartrate isomers containing solutions (pH 12.0 – 13.0; 10 – 30 ° C) depends on the conditions of electroless copper deposition process – under conditions of lower alkalinity and lower temperature the coatings with more developed surfaces were obtained, whereas the increase in solution pH and increment of temperature result formation of smoother copper coatings.
8. The rate of formaldehyde anodic oxidation depends on the following factors: a) solution pH – with the increase in solutions alkalinity (from 12.0 to 13.0), the rate of HCHO oxidation increases on all investigated surfaces of copper coatings; b) conditions of the formation of copper coatings – the highest rate of HCHO oxidation was determined on the surfaces electrolessly obtained at 10 °C and pH 13.0; c) nature of the ligand – the highest rate of HCHO oxidation was found on copper surfaces electrolessly deposited from solutions containing DL-tartrate.

LIST OF PUBLICATIONS

1. E. Norkus, V. Kepenienė, A. Vaškėlis, J. Jačiauskienė, I. Stalnionienė, G. Stalnionis, D. L. Macalady, „*Application of environmentally friendly ligands for alkaline electroless copper plating systems: Electroless copper deposition using trisodium salt of 2-hydroxy-1,2,3-propanetricarboxylic acid as Cu(II) ligand*”. *Chemija* **17**, N 4 (2006) 20-29.
2. E. Norkus, V. Kepenienė, I. Stalnionienė, „*Application of environmentally friendly ligands for alkaline electroless copper plating systems: comparatively study of electroless copper deposition using L-, D- and DL-tartrates as Cu(II) ligands*”. *Chemija* (2012), in press.

CONFERENCE MATERIALS

1. V. Kepenienė, E. Norkus, J. Jačiauskienė, I. Stalnionienė, G. Stalnionis. “*Application of environmentally friendly ligands for alkaline electroless copper plating systems: Electroless copper deposition using citric acid as Cu(II) ligand*”. 9th National Lithuanian Conference “Chemistry 2009” dedicated to 110th anniversary of academician Juozas Matulis. Proceedings Book, Vilnius – Lithuania (2009) 69.
2. V. Kepenienė, E. Norkus, J. Jačiauskienė, I. Stalnionienė, G. Stalnionis, „*Application of environmentally friendly ligands for alkaline electroless copper plating systems: electroless copper deposition using hydroxycarboxylic acid as Cu(II) ligand*“. Conference of Young Scientists “Interdisciplinary investigations in Physical and Technological Science”, Abstracts, Vilnius – Lithuania (2011).
3. V. Kepenienė, E. Norkus, I. Stalnionienė, G. Stalnionis. „*Application of environmentally friendly ligands for alkaline electroless copper plating systems: Electroless copper deposition using isomers of 2,3-hydroxy-1,4-butandicarboxylic acid as Cu(II) ligands*“. 10th International Conference of Lithuanian Chemists “Chemistry 2011” dedicated to International Year of Chemistry 2011. Abstracts, Vilnius – Lithuania (2011) 68.

CHEMINIO VARIAVIMO SISTEMŲ, Cu(II) LIGANDAIS NAUDOJANT HIDROKSIKARBOKSIRŪGŠTIS, YPATUMŲ TYRIMAS

REZIUOMĖ

Cheminio variavimo tirpalai bei cheminio variavimo procesai tiriami jau nuo XX a. vidurio iki šių dienų, ieškant vis efektyvesnių parametrų dangų funkcinėms bei dekoratyvinėms savybėms pagerinti. Pastaruoju metu vis didesnis dėmesys krypta ne tik į nusodinamų dangų funkcionalumą, bet ir į ekologiškai nekenksmingus ar mažiau kenksmingus technologinius procesus, pvz., vykdoma ekologiškai nekenksmingų ligandų paieška. Kaip alternatyva šiuo metu siūlomos dvi cheminių junginių klasės, t.y. alditoliai (polihidroksiliai alkoholiai) ir hidroksikarboksirūgštys.

Pagrindinis darbo tikslas: ištirti cheminio variavimo sistemas ir jose vykstančius procesus, vario(II) jonų ligandais naudojant ekologiškai nekenksmingas citrinų ir vyno rūgštis.

Nustatyta, kad 2-hidroksipropan-1,2,3-trikarboksirūgštis (citrinų rūgštis) ir 2,3-dihidroksibutano-1,4-dirūgštis (vyno rūgštis) šarminėje terpėje sudaro pakankamai patvarius kompleksus su vario(II) jonais ir yra tinkamas ligandas vario(II) kompleksinimui šarminiuose (pH > 12) cheminio variavimo tirpaluose. Ištirta vario(II)-citrato ir Cu(II)-D-, L- ir DL-tartratų kompleksų redukcija hidratuotu formaldehidu, apibūdintos gautosios vario dangos. Optimaliomis proceso vykdymo sąlygomis kambario temperatūroje per vieną valandą gali būti nusodintos kompaktiškos iki ~ 3 μm storio vario dangos. Cheminio variavimo tirpalai buvo stabilūs – jokių Cu(II) redukcijos tirpalo tūryje požymių nepastebėjome.

Ciklinės voltamperometrijos metodu tirta HCHO anodinė oksidacija ant elektrochemiškai ir chemiškai nusodinto vario elektrodo, atlikti Cu elektrodo mišriojo potencialo matavimai vario dengimosi metu.

Gauti rezultatai palyginti su duomenimis, gautais sistemose su kitokiais ligandais. Aptartos ir patikslintos galimos pusiausvyros tirtuose tirpaluose.

Information about the author

Name, Surname	Virginija Kepenienė
Birth date and place	1980 02 15, Rokiškis
Education	
1998	Graduation from „Obelių” Secondary school, Obeliai
1998–2002	Vilnius Pedagogical University, bachelor degree in chemistry and teacher qualification
2002–2004	Vilnius Pedagogical University, master degree in chemistry and teacher qualification
2004–2012	Doctoral studies at the Institute of Chemistry
Work experience	
2003/09–2012/01	Vilnius Pedagogical University, Faculty of Natural Sciences, Department of Chemistry, laboratory technician
From 2012/02	Department of Catalysis, Institute of Chemistry of Center for Physical Sciences and Technology, engineer

Informacija apie autorių

Vardas, Pavardė	Virginija Kepenienė
Gimimo vieta ir data	1980 02 15, Rokiškis
Išsilavinimas	
1998	Obelių vidurinė mokykla, Obeliai
1998–2002	Vilniaus Pedagoginis universitetas, bakalauro laipsnis ir bendrojo lavinimo mokyklos chemijos mokytojo kvalifikacija
2002–2004	Vilniaus Pedagoginis universitetas, magistro laipsnis ir gimnazijos chemijos mokytojo kvalifikacija
2004–2012	Doktorantūros studijos Chemijos institute
Darbo patirtis	
2003/09–2012/01	Vilniaus pedagoginis universitetas, gamtos mokslų fakultetas, chemijos katedra, vyr. laborantė
Nuo 2012/02	VMTI Fizinių ir technologijos mokslų centro Chemijos instituto Katalizės skyrius, inžinierė