



# Formulation and characterization of electrolyte for decorative gold plating based on mercaptotriazole



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## ABSTRACT

A procedure for the formulation and characterization of a gilding electrolyte based on mercaptotriazole is described. It was found that the electrolyte can be synthesized in a wide pH range, so solutions with different pH values (2, 4, 7, 9 and 12) have been prepared and analyzed. Inductively coupled plasma atomic emission spectroscopy and ultraviolet–visible spectroscopy were used for the chemical characterization of the prepared solutions. Electrochemical characterization is performed by open circuit potential measurement, cyclic voltammetry and polarization measurements.

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## 1. Introduction

The electrodeposition of gold is not a new process, but has been widely used in the automotive industry, biomedical processes and electronics industry, such as in computers, telecommunications, and aerospace applications. [1–5]. The combination of excellent electrical conductivity and high corrosion resistance has led to its widespread use as the standard material for interconnections, bond pads, contacts, as well as conductors, electrodes, and other passive components [6].

Electroplated gold can be classified as either soft gold or hard gold [7].

Soft gold electrodeposition has traditionally been performed using gold cyanide or gold sulphite electrolytes. However both of these electrolytes have inherent problems regarding long term sustainability as well as process incompatibility [1–3,8]. This has led to the search for alternative electrolytes [9–11].

Traditionally, gold has been plated from cyanide electrolytes, where (Au<sup>+</sup>) is ligated with cyanide (CN<sup>-</sup>). The cyanide electrolyte is

exceptionally stable with the stability constant of AuCN being 10<sup>38</sup> [6]. However, due to fears about safety and the disposal of process waste, there is a growing concern regarding the use of cyanide-based processes [6,9,10]. The main problem with the use of cyanide electrolytes is their poor compatibility with many standard positive photo resists. The other principal disadvantage of cyanide is its high toxicity [3,8,11,12]. The interest in developing non-toxic gold electrolytes, such as those based on a gold sulphite complex, has grown rapidly in recent years [7,13–17].

Over the past few years there has been some interest in gold deposition from an electrolyte containing two different complexants, sulphite as well as thiosulphate. This electrolyte was originally proposed by Osaka and co-workers who used it to deposit soft gold, which was comparable to gold deposited from a sulphite electrolyte [18–20].

Osaka and co-workers [19,20] investigated the possibility of electroplating soft gold from a thiosulphate–sulphite mixed ligand bath, specifically for application to the formation of micro bumps on silicon wafers. This bath is operated at a slightly acidic pH of 6.0, and at a mildly elevated temperature of 60 °C. It is highly stable, and there is no need to add any stabilizer to suppress spontaneous decomposition. They also added phosphoric acid as a buffering agent and thallium ions to soften the deposits. The desirable attributes of this thiosulphate–sulphite electrolyte was that it was stable at near neutral pH, which provided compatibility with photo resists, and that it was more stable than either gold sulphite or gold thiosulphate electrolytes [21].

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The possibility of electroplating soft gold specifically for the formation of microbumps on silicon wafers from a non-cyanide bath containing both thiosulphate and sulphite as complexing agents was proposed by Osaka and co-workers [19]. Liew, Roy, Scot and Green at Newcastle have developed an electrolyte for soft gold electrodeposition which has attempted to eliminate  $\text{Na}_2\text{HPO}_4$  and  $\text{Ti}^+$  [22].

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi Ltd. [23].

Richter and co-workers [24] developed a thiosulphate–sulphite mixed ligand bath with ascorbic acid as the reducing agent. The possibility of developing these baths was initially investigated based on the well-known mixed potential theory combined with partial polarization curves measured at a gold electrode.

Krulik and Mandich [25] reported that the Au(I) thiosulphate–sulphite mixed ligand system functions as an autocatalytic bath in the absence of any conventional reducing agent. They believed that the thiosulphate–sulphite mixture itself is a reducing agent system, and that sulphite functions as the main reducing agent in this bath.

At the Institute of Mining and Metallurgy Bor a completely new electrolytic bath based on a gold complex with mercaptotriazole was developed and tested. Studies have shown that the new electrolyte can be successfully used in electrolytic baths for hard and decorative plating. Contrary to the previous complexes [26], it retained a sufficient stability in a period of at least three months [27,28].

Detailed investigations were carried out in order to determine the optimum conditions for obtaining quality decorative gold plating from this electrolyte and to compare it with the quality of gold plating obtained from the classic electrolyte [29,30]. Based on experimental investigations, it could be concluded that the quality of decorative gold plating, obtained from a gold complex based on mercaptotriazole, satisfies all requirements of decorative gold plating. The most important advantage of this electrolyte is ecological, as the gold could be regenerated by simply settling with hydrogen peroxide in which the sulphur is precipitated [30].

In this paper we report on: (1) the method of formulation of the electrolytes for decorative gold plating based on a gold complex with mercaptotriazole at different pH levels; and (2) chemical and electrochemical characterization. The gold complexes existing in solution have been examined by UV–vis spectrophotometry and compared with the spectra of other non-cyanide gold complexes. Electrochemical methods are used to determine the characteristics of the electrolyte at different pH.

## 2. Experimental

### 2.1. Chemicals

For the synthesis of the gold complex with mercaptotriazole the following chemicals were used: gold powder (99.99% Mining and Metallurgy Institute Bor); hydrochloric acid p.a. (Zorka, Sabac); nitric acid p.a. (Zorka, Sabac), glycine (min. 99%, Alkaloid Skopje), potassium hydroxide (Merck, Germany), distilled water (5  $\mu\text{S}/\text{cm}$ ) and mercaptotriazole. Mercaptotriazole was synthesized in our laboratory. Thiosemicarbazide,  $\text{CH}_5\text{N}_3\text{S}$  (min 98%, Merck, Germany) and formamide p.a. (Alkaloid, Skopje) were used in this synthesis.

### 2.2. Methods

#### 2.2.1. Raman spectroscopy

Raman spectra of synthesized mercaptotriazole were recorded in the “backscattering geometry”, using a  $\mu$ -Raman system with a Jobin Yvon T64000 three monochromator, and a CCD (charge-coupled-device) detector. As a source for the excitation an

Ar laser 514 nm was used. All measurements were done at a laser power of 80 mW. Raman spectra were recorded in the frequency range 100–3500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### 2.2.2. IR

Analysis of the mercaptotriazole was done by infrared spectrometry using a Perkin-Elmer 983G Infrared spectrophotometer using the KBr technique (finely pulverized sample), in the range 100–4000  $\text{cm}^{-1}$ .

#### 2.2.3. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Produced by: Spectre, Model: Ciris Visio, Detection limit:  $<0.0001 \text{ g}/\text{dm}^3$ ) and Atomic Absorption Spectrophotometer (AAS, Produced by: Perkins & Elmer, Model: 403, Detection limit:  $<0.0001 \text{ g}/\text{dm}^3$ ) were used in order to determine the content of gold in solution.

#### 2.2.4. Ultraviolet–visible spectroscopy

The gold complex in solution was identified using ultraviolet–visible spectroscopy using a Perkin-Elmer Lambda 15 UV–vis spectrophotometer. In these experiments, the spectra were recorded using a standard quartz cuvette with a particular electrolyte, and by performing a fast scan over the wavelength of 190–900 nm.

### 2.3. Electrochemical techniques and procedures

Electrochemical studies were carried out using cyclic voltammetry, open circuit potential measurement and polarization measurements in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was a gold plated platinum electrode (surface 4.522  $\text{mm}^2$ ), whose potential was controlled against the saturated calomel reference electrode (SCE). Platinum foil (1 cm  $\times$  2 cm) served as a counter electrode.

The computerized control (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform and applications specifically developed for electrochemical measurements), fully developed by the Technical Faculty in Bor [31], were used to run the electrochemical experiments. The hardware consisted of a PC, AD/DA converter (PCI-E 20 428 produced by Burr-Brown) and an analog interface developed at the University of Belgrade, Technical Faculty in Bor.

The electrolyte volume used in the experiments was 100 ml. All experiments were carried out at a temperature of  $25 \pm 0.5^\circ\text{C}$ .

The pH and conductivity of the electrolytes were measured before and after each electrochemical measurement.

Before the start of each experiment, the electrochemical cell was rinsed twice with distilled water, and then with working solution.

The open circuit potential was monitored for a period of 60 s.

Cyclic voltammograms were recorded with a scan rate of 100 mV/s, in the following potential ranges:

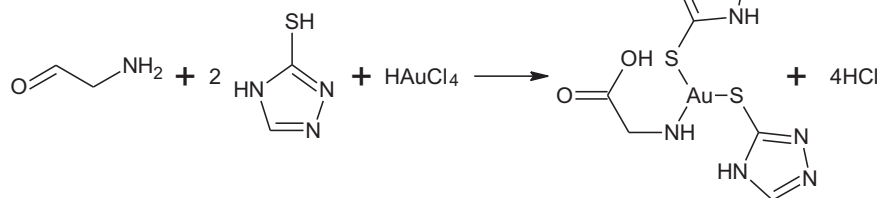
- for pH 2: (+1.6 to  $-0.6$ ) V vs. SCE
- for pH 4: (+1.6 to  $-1.5$ ) V vs. SCE
- for pH 7: (+1.5 to  $-1.3$ ) V vs. SCE
- for pH 9: (+1.2 to  $-1$ ) V vs. SCE
- for pH 12: (+1.5 to  $-1.3$ ) V vs. SCE

Polarization curves were recorded with a scan rate of 5 mV/s in the following potential ranges: for pH 2: (+0.2 to  $-0.6$ ) V vs. SCE; for pH 4: (+0.2 to  $-1.1$ ) V vs. SCE, for pH 7: (+0.2 to  $-1.2$ ) V vs. SCE; for pH 9 and 12 (0.0 to  $-1.3$ ) V vs. SCE.

Potential ranges were ordered by the start of gaseous hydrogen (bottom) and gaseous oxygen (upper limit) evolution.

#### 2.4. Formulation of electrolyte

Under certain conditions gold, from aurochloric acid, reacts with organic compounds glycine and mercaptotriazole ( $C_2H_3N_3SH$ ).



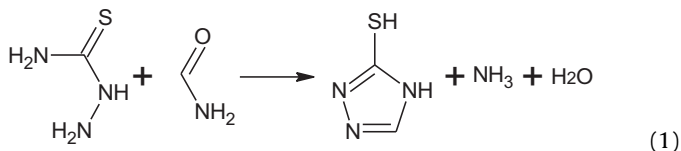
Structurally the same reaction can be presented as follows:

Experimental investigations show that the quality of decorative gold plating, obtained from a gold complex based on mercaptotriazole, can be successfully used in an electrolytic bath for decorative and hard gold plating [30].

##### 2.4.1. Synthesis of mercaptotriazole (MT)

Organic compounds with five member ring structures containing heteroatoms, for example nitrogen, can bind other elements, as can compounds containing an active mercapto group [28].

Mercaptotriazole (MT) is a typical representative of this group of organic compounds, and can be synthesized in several ways. In the present experimental work the method developed by the Beyer and Kroger [32] was used as the simplest one. It is based on the reaction of thiosemicarbazide with formamide:



The reaction mixture in a glass bottle with rectification columns is heated for 20 min at 80 °C. After dissolution, it can be observed that the reaction mixture of thiosemicarbazide and formamide is first dark green, then light green and finally it is pale yellow. The appearance of a pale yellow color indicates the end of the reaction. The content of the glass bottle crystallizes after cooling. For use in galvanic processes, the mercaptotriazole must be recrystallized by dissolving in a mixture of ethyl-alcohol/water (1:3). Recrystallized crystals are rinsed with the same mixture and dried. The melting point of these crystals is 215 °C.

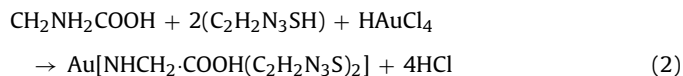
The recorded Raman spectrum of the crystalline MT confirmed the thione form of this molecule, while the IR spectrum of the MT solution provided an evidence of the existence of thione–thiol tautomerism. The IR and Raman spectra are in agreement with the literature data [33–35].

##### 2.4.2. Formulation of gold complex with mercaptotriazole

For the formulation of the gold complex with mercaptotriazole, theoretical and experimental knowledge of obtaining similar complexes of platinum groups of metals was used [36]. In water these metals form color compounds with mercaptotriazole.

By analogy with the structure of corresponding palladium complexes [36] it was assumed that the  $Au^{3+}$  gold builds complex compounds with different ligands around the metal in the center of the molecule. Also, it is assumed that the chemical bond between gold and mercaptotriazole in the electrolyte is achieved by forming a bond over the mercapto-SH groups, while the connection

with glycine is over the amine-NH<sub>2</sub> group. Based on analogy to palladium, the reaction may be shown as follows:



The electrolyte based on the gold complex with mercaptotriazole was prepared by first dissolving gold (Au, 99.99%) in aqua regia (HCl:HNO<sub>3</sub> = 3:1). Dissolution is carried out in a laboratory glass with moderate heating on a sand bath by evaporation until dry. Hydrochloric acid (HCl, 1.19 g/dm<sup>3</sup>) is added to the dry residue and evaporated again until dry. The process is repeated two more times. Distilled water is added to the dry residue and evaporated with the aim to obtain crystals of chloroauric acid (HAuCl<sub>4</sub>). These crystals are dissolved in water.

In this way, the concentration of gold is accomplished to be 2.5 g/dm<sup>3</sup>, which is an optimal parameter for decorative gold coating electrodeposition [30].

The solution of glycine was slowly added to the solution of chloroauric acid in stoichiometric quantity. Adding glycine solution to the chloroauric acid changes the color of the solution from yellow to pale yellow. Further preparation of the bath varies depending on the pH:

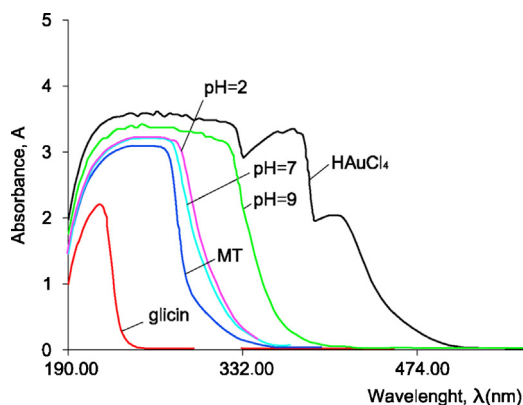
- For a solution of pH 2, MT is added in stoichiometric quantity in the form of 6% solution.
- For solutions of pH 4, 7, 9 and 12, 1 M KOH was first added to the appropriate pH values and then MT in the form of 6% solution was added in stoichiometric quantities.

The pH of the electrolyte was monitored using a pH meter (HANNA-Aldrich Sigma-Model C3724 1EA).

For the creation of this electrolytic bath it is also possible to use sodium hydroxide, but in our research potassium hydroxide was used by analogy with cyanide baths.

The procedure for the preparation of all mentioned baths comprises the addition of glycine before the addition of a 6% solution of mercaptotriazole. The addition of mercaptotriazole to the chloroauric acid and glycine mixture initially leads to the formation of a voluminous precipitate. This precipitate was dissolved by the continuous addition of mercaptotriazole and by adjusting the pH value of the electrolyte. Adding mercaptotriazole to the chloroauric acid and glycine mixture shifts the pH of the electrolyte towards lower values, and it is necessary to add 1 M KOH to control the pH. So the most important aspect during electrolyte formulation was the control of the pH. The color of the precipitate depends on the pH of the electrolyte: at pH 7 it is red, at pH 9 gray, and at pH 12 it is an off-white color.

Potassium hydroxide solution was added until the precipitate was completely dissolved. The chloroauric acid solution, used for the synthesis of the complex, was bright yellow in color. The electrolyte obtained was pale yellow (the color is more intense than the color of the cyanide electrolyte). The intensity of the yellow depends on the pH value of the solution. The electrolyte at pH 2



**Fig. 1.** UV-vis absorption spectra of: glycine (6%), mercaptotriazole (6%), chloroauric acid ( $2.5 \text{ g Au/dm}^3$ ), gold complex with mercaptotriazole with different pH of 2, 7 and 9.

and at pH 12 is colorless, whilst at pH 4 the solution is pale yellow. The intensity of the yellow color of the solution increases at pH 7, and at pH 9 the solution is at its most intense pale yellow color.

### 3. Results and discussion

#### 3.1. Chemical characterization of complexes

Inductively coupled plasma atomic emission spectroscopy was used to monitor the concentration of gold in the electrolytes. This analysis confirmed that the concentration of gold in all synthesized electrolytes was  $2.50 \text{ g/dm}^3$ .

For Au–MT electrolyte chemical characterization, the UV-vis absorption spectra were recorded for the following compounds mentioned above and are presented in plots of absorbance, *A*, against wavelength,  $\lambda$  (Fig. 1).

1. Solution of chloroauric acid with gold concentration of  $2.5 \text{ g/dm}^3$ , pH 1.25
2. Solution of glycine, 6%, pH 7.00
3. Solution of mercaptotriazole, 6%, pH 4.50
4. Gold complexes with mercaptotriazole, with gold concentration of  $2.5 \text{ g/dm}^3$  and pH values of 2, 7 and 9.

The solution of chloroauric acid was used without an adjustment in pH (pH 1.25). The gold complex with mercaptotriazole at pH 2 was also used without pH adjustment.

An absorption peak at 216.8 nm was detected for the glycine solution, which is very close to the literature data for a solution of pH 9 (absorption peak at 210 nm) [21]. For the MT solution (6%, pH 4.50), the absorption peak was detected at 248.8 nm, which is also very close to the available literature data (251 nm) [36].

For the Au(III) chloride solution ( $C_{\text{Au}} = 2.5 \text{ g/dm}^3$ ), several peaks were detected: 239.2 nm, 251.2 nm, 263.2 nm, 273.6 nm, 284.8 nm, 297.6 nm, and 308.8 nm, followed by shoulders at: 374.4 nm and 406.4 nm. Liew et al. [21] detected an absorption peak at 210 nm for an  $\text{HAuCl}_4$  solution containing 0.6 mM Au(III) ions, followed by a shoulder at 280 nm. Some other authors detected absorption peaks at 240 nm and 313 nm [37–39]. These differences are probably due to the differences in concentration of Au(III) chloride salts, as well as in the pH values.

The values of 257.6 nm and 253.6 nm, for the absorption peaks of the Au–MT electrolytes obtained at pH 2 and pH 7, respectively, were very close to the absorption peak of MT (248.8 nm), while the Au–MT electrolyte at pH 9 exhibited an absorption peak at 272.0 nm, which may suggest that the bond between MT and Au has only realized in this particular case.

As the value of 272.0 nm lies in the area of the absorption peaks of gold sulphite solution (270 nm), gold thiosulphate solution (285 nm) and gold thiosulphate–sulphite solution (283 nm) [21], it may be assumed that the coordination of Au to MT at pH 9 is realized through the sulphur atom. This is in accordance with the findings of Wrzosek and Bukovska [33]. They found that AMT was adsorbed on Ag and Au surfaces by forming a thiolate bond with the metal; this fact was confirmed by the results obtained from the SERS and XPS experiments. However, they noted that the AMT molecules may also interact with the surface through the nitrogen atoms of the deprotonated triazole rings, oriented flat to the metal surface. In the subsequent steps of monolayer formation, the AMT molecules may change their orientation with respect to the surface, followed by the simultaneous protonation of the nitrogen in the ring. This structure is usually stabilized by a network of hydrogen bonds and interactions of the aromatic rings oriented parallel to each other. Obviously, two different structures of the AMT monolayers are possible. Wrzosek and Bukovska concluded that the relative amount of the respective structure depends on the concentration of adsorbate in the solution and its pH value, and that the monolayer structure can be reversibly tuned between the two molecular states by changing one or both of these parameters. XPS experiments proved the existence of a Metal–S bond in all conditions in the monolayer's of both forms of compound [33].

It is possible that the MT ring orientation in the early phase of our work is more or less perpendicular to the metal surface due to the low pH value of the solution; in these circumstances the hydrogen atom attached to the pyrrole nitrogen atom stays retained. The close values for the absorption peaks for the MT and Au–MT electrolyte at pH 2 suggest that the bound Au–S is very weak, almost insignificant. Wrzosek and Bukovska showed that an increased pH value of the solution is favorable to ring deprotonation. The change in ring orientation to one that is more parallel with respect to the metal surface is accompanied by the transformation of the chemical state. Following these facts, it may be speculated that there is the possibility that MT molecules at pH 9 may interact with the surface through the sulphur, but also through the nitrogen atoms of the deprotonated triazole rings, oriented flat to the metal surface. This complicated coordination of Au to MT at pH 9 may be supported by the shifting of the MT absorption peak from 248.8 nm to 272.0 nm.

All this supports our previous findings that the electrolyte based on a gold complex with mercaptotriazole at pH 9 is the most stable, and the gold coatings obtained from this electrolyte provide the best characteristics [40].

#### 3.2. Electrochemical experiments

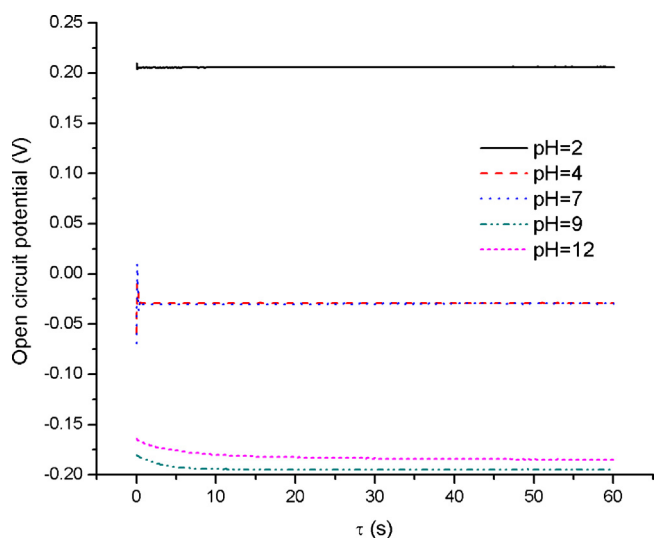
Subsequent studies were carried out with the aim of investigating the electrochemical characteristics of the synthesized electrolytes over the whole stability range (pH 2–12) at the optimal concentration of gold in the electrolyte of  $2.5 \text{ g/dm}^3$  [26,36]. Electrochemical characterization of the complex was conducted by measuring the conductivity of the electrolyte, the open circuit potential measurements, by cyclic voltammetry and by the recording of polarization curves. Conductivity and pH of the electrolytes were measured before and after each polarization.

##### 3.2.1. Open circuit potential

The change in open circuit potential of gold in solutions with pH values of 2, 4, 7, 9 and 12 was monitored over 60 s. Fig. 2 and Table 1 show the values of the open circuit potential and pH of the electrolytes before and after electrochemical polarization measurements. Measurements were performed on freshly prepared electrolytes.

Fig. 2 and Table 1 show that with an increase in the pH of the electrolyte, the open circuit potential shifts to more negative values.





**Fig. 2.** Open circuit potential for electrolytes with different pH values and a gold concentration of  $C = 2.5 \text{ g/dm}^3$ .

The most negative OCP of  $-0.194 \text{ V}$  vs. SCE was measured at pH 12, while the most positive value was obtained at pH 2 ( $+0.206 \text{ V}$  vs. SCE). At pH 4 and pH 7 the measured values of the open circuit potential are almost equal:  $-0.028$  or  $-0.029 \text{ V}$  vs. SCE. At pH 9 the measured OCP value was  $-0.185 \text{ V}$  vs. SCE.

The most positive potential value obtained at pH 2 indicates that the gold in this solution is in the least stable complex, providing the highest concentration of free gold ions. Potential changes with the change in pH indicate a change in the type of connection of the gold ions with the other species present in the electrolyte. This is in agreement with the conclusions derived on the basis of spectroscopic measurements—more negative value of the potential at higher pH values means that the stability of the form in which gold occurs increases with increasing pH.

From Fig. 2 it can also be noted that the stable value of OCP in acidic and neutral media was established almost immediately (in the first second) after the immersion of the electrode. In alkaline solutions the establishment of the stable open circuit potential lasted more than 10 s, which indicates that the establishment of a stable structure of the electrochemical double layer included the slow diffusion of larger particles, their adsorption and desorption as well as the possible competitive adsorption.

After electrochemical polarization measurements the pH values of the acidic electrolytes increased, while in alkaline media it decreased, as shown in Table 1. Minor changes in pH value were observed at pH 7 (from 7.10 to 7.05) and the greatest at pH 12 (from 11.80 to 11.35).

The decreasing in pH in alkaline solutions is a consequence of oxygen evolution due to the oxidation of hydroxyl ions:



**Table 1**

Steady state values of open circuit potential and pH values of electrolyte before and after polarization measurements (p.m.).

Predicted pH	2	4	7	9	12
Measured pH before p.m.	1.85	4.20	7.10	8.96	11.80
Measured pH after p.m.	1.95	4.40	7.05	8.85	11.35
Open circuit potential (V vs. SCE)	+0.206	-0.028	-0.029	-0.185	-0.194

Reaction (4) in these cases consumes more electricity than hydrogen evolution in the observed experiments:



As a result, more hydroxyl ions are consumed by reaction (4), than are produced in reaction (5).

In contrast, in acidic solutions the reaction consuming hydrogen ions dominates over oxygen evolution. In alkaline medium these reactions are:



The increase in pH after polarization measurements in acid solutions proves that hydrogen is released in parallel with the deposition of gold. This leads to a decrease in the current efficiency, and the quality of the gold plate is worse than that obtained from the electrolyte at pH 9.

### 3.2.2. Cyclic voltammetry

Cyclic voltammograms recorded at different pH values of the electrolyte (pH 2, 4, 7, 9 and 12) are shown in Fig. 3. For a better view, the cyclic voltammograms are shown in three diagrams (Fig. 3a–c). Cyclic voltammograms for electrolytes at pH 2 and 4 are shown in Fig. 3a. In Fig. 3b the cyclic voltammogram for an electrolyte with pH 7 is presented, and in Fig. 3c cyclic voltammograms for electrolytes at pH 9 and 12 are given.

From the cyclic voltammograms for electrolytes with different pH values recorded with a potential scan rate of  $100 \text{ mV/s}$  presented in (Fig. 3a–c), it can be noted that with an increase in pH the cathodic current waves shift to more negative potentials.

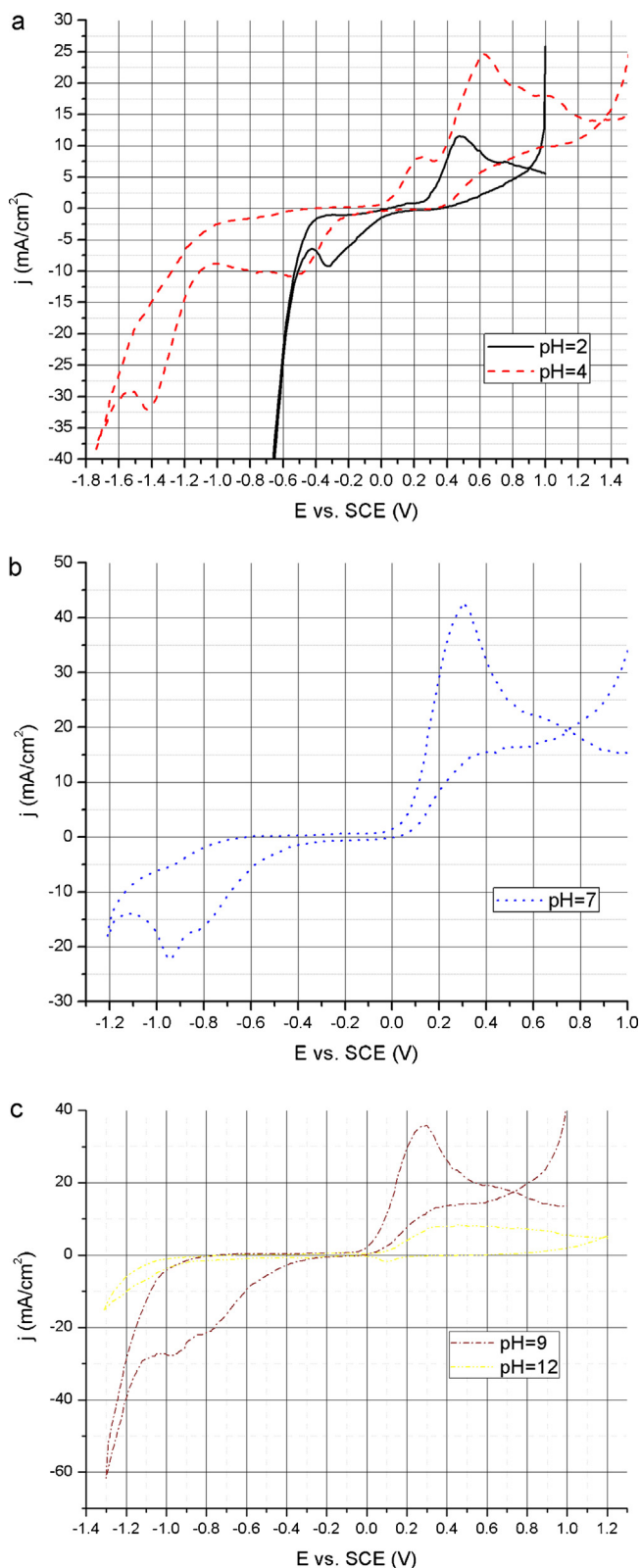
In the anodic part, all the voltammograms are of a similar shape. The current density for pH 7 is the smallest over the whole course of the curve. The voltammogram recorded for the electrolyte of pH 2 is significantly different to the others, because in its cathodic part a sharp current peak appears at a potential of about  $-0.15 \text{ V}$  vs. SCE, and from  $-0.5 \text{ V}$  vs. SCE the cathodic current begins to rise sharply, indicating the beginning of gaseous hydrogen evolution. The voltammogram of the sample at pH 4 has two cathodic peaks. The first peak is on the potential of  $-0.58 \text{ V}$  vs. SCE and the second on the potential of  $-1.48 \text{ V}$  vs. SCE, and from  $-1.55 \text{ V}$  vs. SCE the cathodic current begins to rise, which also indicates gaseous hydrogen evolution.

On the cathodic part of the voltammograms recorded for the alkaline electrolytes (pH 9 and 12) no clear current peak appears, only folds in the locations corresponding to the reaction of gold reduction. However, there are major differences between the voltammograms for electrolytes with pH 9 and pH 12. Anodic and cathodic current densities are several times higher at pH 9, and the current waves on the cathodic part of the curve are at considerably more positive potentials, although the open circuit potentials for the two electrolytes are approximately equal. This indicates a lower overvoltage, i.e. less energy consumption in the process of gold electrodeposition.

### 3.2.3. Polarization curves

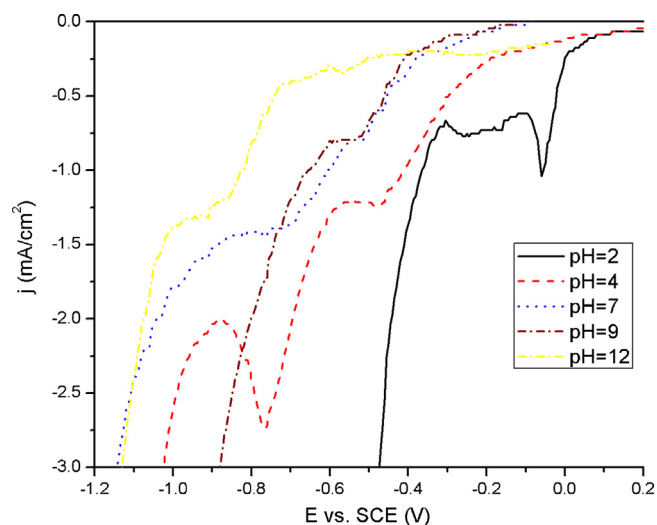
Polarization curves for the electrolyte with a gold concentration of  $2.5 \text{ g/dm}^3$  recorded at different pH values with a potential scan rate of  $5 \text{ mV/s}$  are presented in Fig. 4. From these curves the limiting current densities can be determined.

The limiting current is an important parameter for the characterization of electrochemical systems. Two plateaus, the first being wide and the second narrower, are observed on the polarization curves. The first plateau current density is lowest in the electrolyte with a pH value of 9 and highest for the electrolyte with a pH value



**Fig. 3.** Cyclic voltammograms of electrolytes with a gold concentration of 2.5 g/dm<sup>3</sup> at different pH values: (a) pH 2 and 4; (b) pH 7; (c) pH 9 and 12.

of 12. The values of the potential at which the limiting current densities were reached are also different. The first plateau current densities range from 0.02 mA/cm<sup>2</sup> (obtained for pH 9 and pH 7) to 0.16 mA/cm<sup>2</sup> (obtained for pH 12). The first plateau current densities for electrolytes with pH 2 and pH 4 are almost equal, in the



**Fig. 4.** Polarization curves for an electrolyte with a gold concentration of 2.5 g/dm<sup>3</sup> at pH 2, 4, 7, 9 and 12.

range of 0.06 mA/cm<sup>2</sup>. Limiting current density values were higher than the ones for cyanide (0.05 A/dm<sup>2</sup>), and similar to the values of the limiting current density for the other non-cyanide electrolytes [21].

#### 4. Conclusion

This paper presents a method for the formulation of an electrolyte based on mercaptotriazole, which could be used for decorative plating baths, as well as its chemical and electrochemical properties. UV–vis spectroscopy showed that the spectra of the gold complex at pH 2 and pH 7 show very similar absorption profiles. At pH 9, the absorption peaks in spectrum appear at longer wavelengths, close to the wavelengths for other non-cyanide electrolytes. The open circuit potential is the most positive at pH 2. With an increase in pH the OCP value becomes negative, indicating the binding of gold in the form of stable complexes. Chemical and electrochemical methods are in agreement with conclusion that the bond between gold and mercaptotriazole is the strongest at pH 9, and that at this pH the complex is the most stable. Also, the lowest value of limiting current density was observed for the electrolyte at pH 9. Cyclic voltammograms and polarization curves explain the reasons for the observed trends in gold coatings obtained from electrolytes based on mercaptotriazole where a value of pH 9 has resulted in the best characteristics, which were comparable to gold coatings obtained from cyanide electrolytes.

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