VOLTAMMETRY OF AQUEOUS CHLOROAURIC ACID WITH HANGING MERCURY DROP ELECTRODE

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Dedicated to the 90th anniversary of polarography.

In d.c. voltammetry of dilute aqueous chloroauric acid with hanging mercury drop electrode, when potential scanning proceeds from negative to positive values, a prominent maximum of cathodic current appears on the curve near 0 V. The effect is explained as due to catalytic evolution of hydrogen on the electrode initially covered by adsorbed Au-hydroxidic layer. Once the layer dissolves in the acidic solution during the positive scan, a fast evolution of hydrogen takes place, catalysed by short-lived adsorbed gold particles.
Keywords: Aqueous chloroauric acid; Hanging mercury drop electrode; Linear voltammetry; Catalytic hydrogen evolution; Voltammetry; Gold; Hydrogen.

From solutions of electroactive compounds containing gold, the metal is deposited at negative potentials. The solubility of gold in mercury is relatively good[1,2], and when the cathode is mercury, the deposit is gold amalgam which contains more than three different gold-mercury intermetallics[3]. In electrolysis of dilute aqueous chloroauric acid ($HAuCl_4$) at high negative potentials, the reduction of chloroauric anion

$$AuCl_4^- + 3\ e \rightarrow Au + 4\ Cl^- \qquad (1)$$

is accompanied by reduction of hydrogen ion from the acid which alkalizes the electrode/solution interfacial layer

$$H_3O^+ + 2\ e \rightarrow H_2 + OH^-. \qquad (2)$$

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It is known that increasing pH of $HAuCl_4$ solutions causes hydrolytic ligand substitution forming hydroxocomplexes[4]. The hydrolysis of $AuCl_4^-$ ions in pH range 2.25–3.11 increases from 6.45 to 23.3%. The hydroxocomplexes of gold in solutions of this pH region are $[AuCl_3OH]^-$, $[AuCl_2(OH)_2]^-$, $[AuCl(OH)_3]^-$ and $Au(OH)_3$. When pH exceeds 3, the most stable form of Au(III) is its insoluble hydroxide $Au(OH)_3$ which exists in solution medium up to approximately pH 9.5. Species $Au(OH)_3$ aggregates into polymeric colloidal 80–200 nm particles[4] which get adsorbed at the electrode surface. When hanging mercury drop electrode is then polarized from negative to positive potentials, an unusual effect occurs towards the end of the voltammetric curve – a prominent maximum of cathodic current appears at potentials near zero which can be explained as a special case of catalytic evolution of hydrogen.

Catalytic effects in electrochemistry are often used for study of electrode reactions or for analytical purposes[5]. Mercury electrodes are often applied for studying catalytic evolution of hydrogen, but recently in many cases also various amalgam electrodes proved useful for that purpose[6–9]. Compact gold and gold amalgams usually do not catalyse hydrogen evolution – they rather block that process[10], but nanosized gold particles are known for their catalytic properties in heterogeneous systems, also in electrochemistry[11].

EXPERIMENTAL

Voltammetric measurements were carried out using computer-driven Eco-Tribo Polarograph PC-ETP (Polaro-Sensors, Prague, Czech Republic) with MultiElchem v.2.1 software (J. Heyrovský Institute of Physical Chemistry of AS CR, v.v.i.). Hanging mercury drop electrode (HMDE, surface area 0.62 mm^2) and mercury meniscus-covered gold solid amalgam electrode (m-AuSAE)[8,12] with disc diameter 0.40 mm and meniscus surface 0.25 mm^2 were used as working electrodes. Saturated calomel electrode (SCE) based on silver solid amalgam[13] (which has the same potential as classical SCE) was applied as reference electrode. Platinum wire (1 mm diameter and 15 mm length) was used as auxiliary electrode. Prior to voltammetric measurements purified nitrogen had been passed through the solutions for a period of 300 s, and then nitrogen atmosphere was maintained above the solution in the cell. Before each registration of a voltammogram the solution was allowed to rest for 20 s. All measurements were done at room temperature (ca. 22–25 °C). Deionized water produced by Milli-Qplus system (Millipore) was used for preparing solutions, all chemicals used were of p.a. purity.

RESULTS AND DISCUSSION

We found that the limiting current of hydrogen ion was not observed (Figs 1–4), although we polarized the electrode to negative potentials where hydrogen development takes place. We followed behaviour of the maximum of cathodic current appearing at positive potentials, which is connected with hydrogen ion reduction, but which is considerably smaller than the "normal hydrogen wave". Figure 1 shows a cyclic voltammetric curve of a

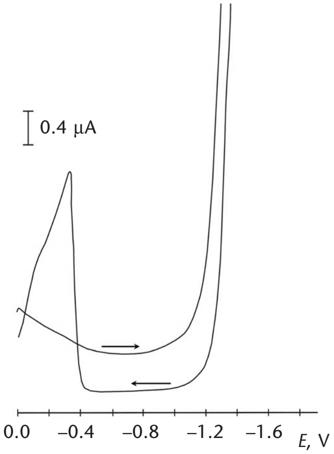

FIG. 1
Cyclic voltammogram of aqueous 1×10^{-4} M $HAuCl_4$ solution (pH 1.9), recorded with delay of 60 s at reverse potential; E_{in} = 0 mV, E_{rev} = –1900 mV, v = 200 mV s^{-1}

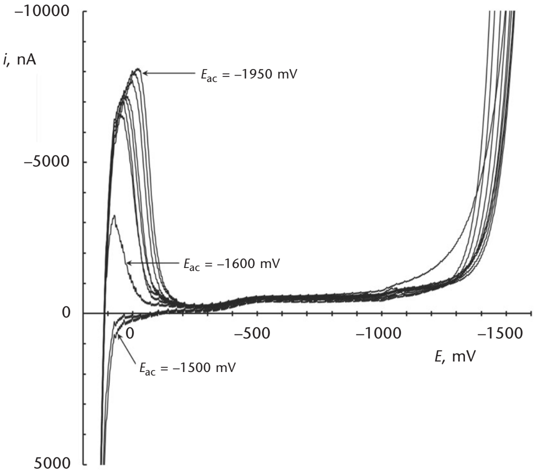

FIG. 2
Linear voltammograms of aqueous 2×10^{-4} M $HAuCl_4$ solution (pH 1.9), recorded from different negative potentials (E_{in} = –1500, –1550, –1600, –1650, –1700, –1750, –1800, –1850, –1900, –1950 mV) to potential E_{fin} = +150 mV with accumulation time t_{ac} = 30 s at E_{in} and with rate of potential scan v = 1000 mV s^{-1}

dilute aqueous chloroauric acid recorded from 0 to –1900 mV and back with hanging mercury drop electrode. At the positive end of the reverse branch of the curve appears a prominent maximum of cathodic current. As in the positive region of the beginning of the curve occurs only inconspicuously decreasing cathodic current, the cause of the steep maximum of cathodic current at the end of the curve is presumably connected with processes occurring in the negative potential range of scan reversal. Preliminary experiments have shown that the maximum of cathodic current depends on the value of the negative potential reached, on the time of delay of potential at the negative limit, on the rate of potential scan, and on pH of the solution. These findings have been thoroughly tested with single-sweep linear voltammetry scanned from negative to positive potentials (Figs 2–5). The positive cathodic current maximum appears towards the end of the scan when the initial potential is at least –1600 mV, and with its more negative values the maximum increases and shifts to negative potentials (Fig. 2). Similar dependence is obtained when the rate of scan from negative to positive potentials is increased, as shown in Fig. 3. Repeated measurements were best reproduced when the initial potential was –1700 mV and the rate of scan was 200 mV s^{-1}. These parameters were then used as standard procedure in further experimental work. When the time of delay of the scan at the initial negative potential, i.e. the time of accumulation of reaction

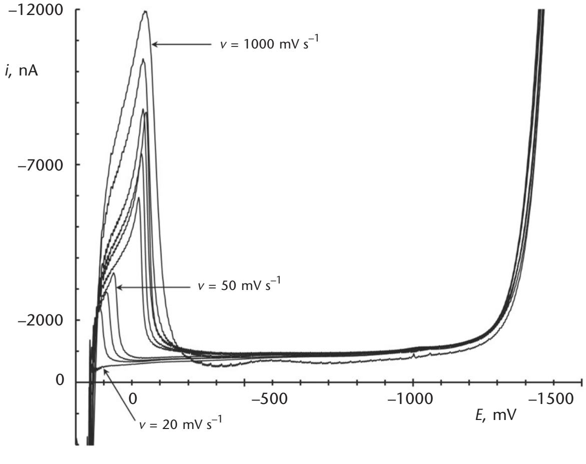

FIG. 3
Linear voltammograms of aqueous 2 × 10^{-4} M $HAuCl_4$ solution (pH 1.9), recorded from E_{in} = –1700 mV to E_{fin} = +150 mV with accumulation time t_{ac} = 10 s with rates of potential scan v = 20, 30, 40, 50, 100, 150, 200, 250, 500, 1000 mV s^{-1}

products at the electrode, is increased, the height of the positive maximum increases, the effect shifts towards negative potentials, and the slope of the charging current part of the curves decreases (Fig. 4). The latter dependence is typical for processes accompanied by adsorption of reaction products at the electrode surface. The cathodic maximum does not appear with short time of accumulation (1–2 s) and the slope of the charging current part of the curve is not affected; then with increasing accumulation time (3–30 s) the peak appears, increases and shifts to negative potentials, and the slope of the charging current part of the curve decreases. Further the height of the maximum and its potential reach their limits and the charging current part of the curve is at minimum, which indicates that total electrode surface is covered by the reaction products. The range of pH of the solutions in which the maximum appears is narrow – between 1.9 and 3. With decreasing acidity, the slope of the charging current part of the curves decreases (Fig. 5). The whole effect depends on the state of the electrode surface: after addition of KCl to 0.01 M concentration to the 2×10^{-4} M $HAuCl_4$ solution, the height of the maximum decreases by about 16% from the value obtained in pure 2×10^{-4} M chloroauric acid; in 2×10^{-4} M $HAuCl_4$ + 0.1 M KCl the chloride anions, which adsorb on mercury at the positive side of the point of zero charge, suppress the maximum completely.

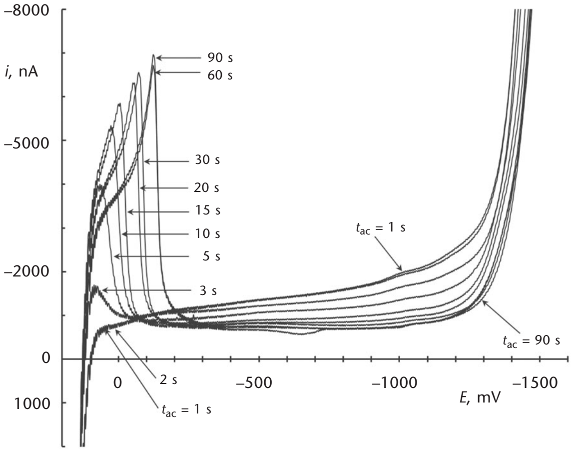

FIG. 4
Linear voltammograms of aqueous 2×10^{-4} M $HAuCl_4$ solution (pH 1.9), recorded from E_{in} = –1700 mV to E_{fin} = +150 mV at rate of potential scan v = 200 mV s^{-1} and with accumulation times t_{ac} = 1, 2, 3, 5, 10, 15, 20, 30, 60, 90 s

The above presented experimental results lead us to their tentative interpretation by considering the complex time-dependent surface processes occurring at the electrode. At negative potentials the mercury drop electrode undergoes simultaneously two electrolytic reactions of the chloroauric acid: reduction of hydrogen ions from the acid and reduction of gold from its anion. The first reaction causes alkalization of the electrode/solution interface which leads to local gradual formation of hydroxocomplexes of gold and ultimately of insoluble hydroxide $Au(OH)_3$, which aggregates into polymeric particles, adsorbed at the electrode surface[4]. That layer decreases the electrode capacity, as is evident from the slopes of the charging current part of the curves (Fig. 4). The second reaction, reduction of gold from the chloroauric anion and from its hydroxocomplexes, occurs within the adsorbed hydroxidic layer, and the gold atoms are electrodeposited at the outer side of the mercury surface prior to their amalgamation. When the electrode potential is then scanned in positive direction, the alkalization of the interface and the formation of gold hydroxide layer ceases, and the hydroxidic layer gradually dissolves in the acidic solution. At the same time ceases also the electrodeposition of gold at the mercury electrode and the

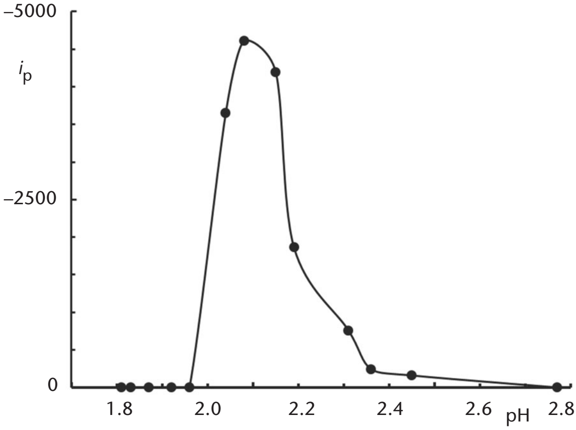

FIG. 5
Dependence of height of the positive cathodic current maximum on pH. Linear voltammograms of aqueous 2×10^{-4} M $HAuCl_4$ + 1×10^{-2} M KCl solutions, recorded from E_{in} = –1700 mV to E_{fin} = +150 mV with accumulation time t_{ac} = 30 s and potential scan rate v = 200 mV s^{-1}; pH values 1.81, 1.83, 1.87, 1.92, 1.96, 2.04, 2.08, 2.15, 2.19, 2.31, 2.36, 2.45, 2.77 gradually increased by regular additions of 0.1 ml 0.1 M NaOH to 10 ml of the initial solution

gold atoms at the electrode surface first quickly temporarily aggregate into adsorbed gold nanoparticles before they get amalgamated. Then in the moment when the layer of gold hydroxide disappears from the electrode surface, the adsorbed gold nanoparticles catalyze evolution of hydrogen[11]. The catalysis occurs at potentials more positive than electrochemical hydrogen evolution at a normal gold amalgam electrode[8]. After some time all the gold particles completely dissolve in mercury electrode, forming gold amalgam. At electrodes prepared from gold amalgams no catalytic evolution of hydrogen was observed[6]. The effect of the rate of sequence of events at the electrode surface depends on the rate of potential scan – at the rate of 20 mV s^{-1} and lower the fast time-dependent processes are quickly over, the surface catalyst becomes amalgamated and the positive cathodic current maximum does not appear (Fig. 3).

CONCLUSION

Voltammetry with hanging mercury drop electrode of aqueous solutions of chloroauric acid confirms that two electrode processes occur simultaneously at negative potentials: evolution of hydrogen and production of gold atoms. These two reactions under experimentally adjusted time and potential conditions lead to generation of cathodic current maximum at positive potentials, which is due to catalytic evolution of hydrogen by short-lived gold nanoparticles.

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