

VOLTAMPEROMETRY (POLAROGRAPHY) OF TRIVALENT GOLD ON SOLID ELECTRODES

O. L. Kabanova

V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry,
Academy of Sciences, USSR, Moscow

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Many articles have been devoted to the polarographic determination of gold in solution on solid electrodes [1-5]. Using a platinum microdisc rotating electrode at an electrode potential $\varphi = 0.6$ V relative to the saturated calomel electrode (S. C. E), it is possible to determine trivalent gold in solution at the lowest limiting concentration of $3 \cdot 10^{-6}$ M [5] on the basis of its cathodic limiting current. In the form of its chlorauric complexes, gold is determined in a supporting electrolyte from electrolytes which do not form complexes with trivalent gold. Of the polarographic methods for determining gold on a dropping mercury electrode (see e.g., review [6]), the methods which have the highest analytical possibilities are those in which gold is determined polarographically in a supporting electrolyte of ethylenediamine and its salts with anionic-addenda [7-14]. Trivalent gold forms a complex with one and two molecules of ethylenediamine [7, 15]. In a 0.1 M KCl supporting electrolyte [7] a wave for the cathodic reduction of trivalent gold from the complex is observed, which is accompanied by anodic dissolution of mercury. According to recent results [13] it is the complex of gold with one molecule of ethylenediamine that is reduced on the cathodic wave. At Cl^- concentrations less than $3 \cdot 10^{-3}$ M only the limiting diffusion current is observed.* The half-wave potential $E_{1/2}$ varies from 0.10 to -0.08 V relative to the S. C. E on changing the pH of the solution and the concentration of ethylenediaminetartrate [8, 9]. On taking polarograms on a mercury cathode in anhydrous ethylenediamine containing 0.1 N NaNO_3 , a clearly defined reversible wave is observed for Au^{III} with $E_{1/2} = -0.74$ V relative to the normal calomel electrode [14]. Unfortunately this last value of $E_{1/2}$ cannot be used for direct comparison with aqueous solutions; the author has pointed this out. It is not possible to come to any definite conclusions on the basis of other investigations regarding the reversibility of the reduction of the complex of Au^{III} with ethylenediamine on a mercury cathode. Consequently there is no information on the standard potential of the system $\text{Au}/\text{Au}^{\text{III}}$ - ethylenediamine complex, and on the instability constants of the ethylenediamine complexes of gold.

We set out to examine the possibility of carrying out polarographic determination of low concentrations of trivalent gold in a supporting electrolyte of 0.5 M ethylenediamine tartrate, using gold and platinum rotating disc electrodes.

Method. A 0.5 M solution of ethylenediamine tartrate was prepared by mixing ethylenediamine, which had been redistilled beforehand in a quartz apparatus, and a solution of tartaric acid in twice distilled water. The tartaric acid was recrystallized from twice distilled water. A solution containing 1.2 mg Au/ml was prepared by dissolving a tared piece of gold foil in aqua regia (the nitric and hydrochloric acids were distilled twice in quartz apparatus), followed by repeated evaporation of the solution with hydrochloric acid, and final dissolution of the dry residue in 1 M HCl. Test solutions of gold were prepared by diluting aliquots of the hydrochloric acid solution of chlorauric acid with 0.5 M ethylenediamine tartrate solution.

pH was measured by means of a glass electrode and an LP-4 potentiometer. A pH of 4.4 was found for all the solutions.

Rotating disc electrodes made from gold (surface area 0.058 cm^2) and platinum, marked "extra" (surface area 0.126 cm^2), were used as the electrodes for taking polarograms. The speed of rotation of the electrodes was varied from $m = 1000$ to $m = 15,000$ rpm and was measured with a VNISI strobometer. A platinum platinized wire immersed in the same solution was used as the other electrode.

* At high Cl^- concentrations a kinetic current is observed.

Polarograms were taken on a Heyrovsky polarograph. The rate of potential change was 200 or 400 mV/min. Polarograms were taken at $25^\circ \pm 0.1^\circ$ in a purified nitrogen atmosphere.

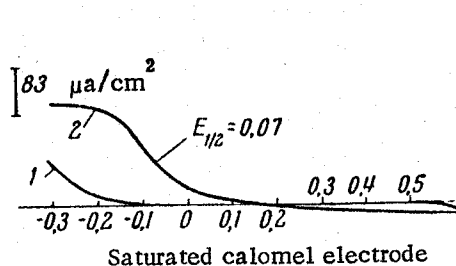


Fig. 1. Curve 1) Polarogram of 0.5 M ethylenediamine tartrate solution on a gold electrode; curve 2) ditto, in the presence of 10^{-4} M Au^{III} .

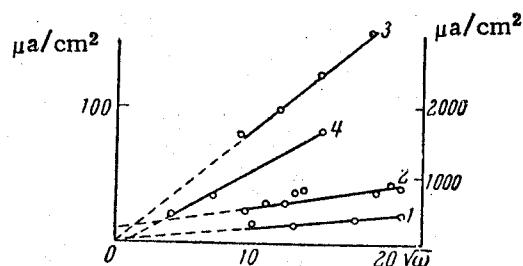


Fig. 2. Curves relating limiting diffusion currents i_{limit} of the Au^{III} complex and $\sqrt{\omega}$ for the following gold concentrations in solution: 1) $4.3 \cdot 10^{-6}$ M; 2) $9.75 \cdot 10^{-6}$ M; 3) $8.6 \cdot 10^{-5}$ M; 4) $2.5 \cdot 10^{-4}$ M.

metallic gold appears on the electrode during this process; consequently, in the final count, reduction occurs with participation of three electrons.

In the case of the experiments illustrated by curves 1 and 2 in Fig. 2, the solutions did not contain hydrochloric acid which was not bound initially into the complex with gold, while in the case of the experiment whose results are illustrated by curve 3, the hydrochloric acid concentration was about 0.04 M.

Figure 3 shows, on a logarithmic scale, the curves relating the values of the limiting current at a constant rotational speed and the trivalent gold concentration of the solution. The curves remain linear on changing the gold concentration by two orders ($4 \cdot 10^{-6}$ to $4 \cdot 10^{-4}$ M).

On the basis of the experimental results we calculated the diffusion coefficient of the gold complex reduced at $\varphi = -0.2$ V relative to the S.C.E. It was assumed that $n = 3$. Levich's formula [16] was used. In order to carry out these calculations we measured the viscosity of the test solutions by means of an Ostwald viscometer; the viscosity was found to be 0.0118 poise. For solutions of $4 \cdot 10^{-6}$ and 10^{-5} M Au^{III} in 0.5 M ethylenediamine tartrate at 25° , the diffusion coefficient was found to be $0.7 \cdot 10^{-5}$ cm²/sec. For comparison we should point out that the diffusion coefficient has been determined polarographically on a dropping mercury electrode, in 0.1 M KCl at a concentration of the complex of trivalent gold with ethylenediamine of $5 \cdot 10^{-4}$ M, and was found to be $0.72 \cdot 10^{-5}$ cm²/sec [7]. Within the limits of experimental accuracy these values coincide.

In solutions having a trivalent gold concentration greater than or equal to 10^{-4} M, at rotational speeds of the electrode of $m = 1000$ -3000 rpm and at $\varphi = -0.2$ V, currents are obtained which are 2-4 times less than the limiting currents calculated on using the value of the diffusion coefficient found. It is possible that the slowing down of the reaction is caused by the presence of $4 \cdot 10^{-2}$ M hydrochloric acid (the effect of hydrochloric acid at concentrations

Gold electrode. Polarograms of solutions of trivalent gold in 0.5 M ethylenediamine tartrate were taken at Au concentrations ranging from $4.3 \cdot 10^{-6}$ to $4 \cdot 10^{-4}$ M. About 50 ml of solution was taken for a polarogram. A typical polarogram is shown in Fig. 1, curve 2. Curve 1, Fig. 1 is the polarographic curve of the supporting electrolyte - 0.5 M ethylenediamine tartrate free from gold ions - on a gold electrode.

As Fig. 1 shows, when gold ions are present and when a gold rotating disc electrode is used, a cathodic polarographic wave with a clearly defined limiting current is observed at a potential of $\varphi = -0.2$ V relative to the S. C. E. and at more negative potentials. The half-wave potential was found to be $E_{1/2} = -0.07$ V. On plotting the polarograms obtained within the coordinates, "potential-logarithm of current density," the wave breaks down into two or three stages with half-wave potentials which differ from each other by 20-60 mV; this indicates that there is a possibility that the reduction of Au^{III} proceeds via its different valence state. Since these half-wave potentials are so close to each other, there is no point in making a detailed analysis of these stages.

It follows from the polarograms that it is best to determine the limiting current of the gold ions at $\varphi = -0.2$ V relative to the S.C. E. Figure 2 shows the relationship between the currents measured at this potential (after correcting for the supporting electrolyte current) and the square root of the angular rotational speed of the electrode $\omega = 2\pi$ m/60 rev/sec. The supporting electrolyte current remains constant with changes in rotational speed. Curves 1, 2, and 3 show the linear relationship between the values of the current density and the square root of ω ; this indicates a diffusion character for the reduction of the gold complex at $\varphi = -0.2$ V. A deposit of

greater than 10^{-3} M on the discharge of the complex of gold with ethylenediamine, as mentioned already, was detected in experiments with a mercury cathode [13]). In general, during cathodic determination of trivalent gold one should avoid the presence of free Cl^- ions, since they sharply increase the supporting electrolyte current, and make it dependent on stirring even at such low chloride concentrations as $5 \cdot 10^{-7}$ M.

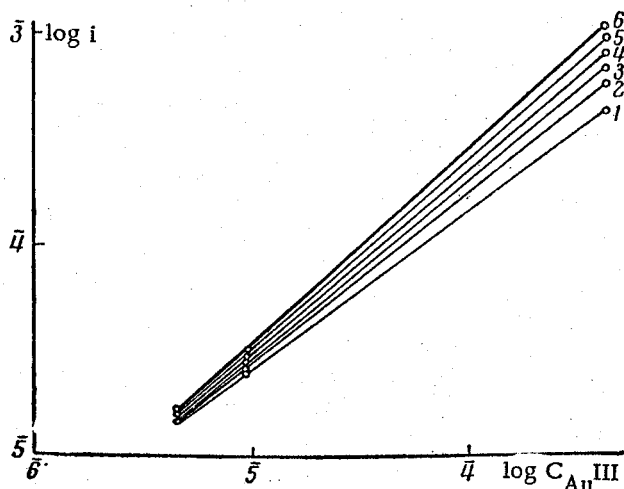


Fig. 3. Curves relating i_{limit} and Au^{III} concentration for the following $\sqrt{\omega}$ values. 1) 10; 2) 11; 3) 12; 4) 13; 5) 14; 6) 15.

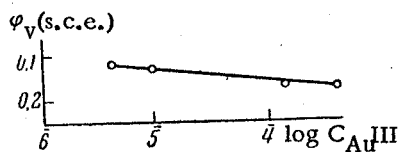


Fig. 4. Potential of the gold electrode as a function of Au^{III} concentration in 0.5 M ethylenediamine tartrate solution.

We measured the potential of the gold electrode in the test solutions without passing a current. The values obtained are given in Fig. 4. On increasing the gold concentration ten times the potential of the gold electrode becomes more positive by 0.027 V. The slope of the $E - \log C_{\text{Au}^{\text{III}}}$ curve is increased above the theoretical value (0.0195 V at 25°) as a result of the reduction of Au by ethylenediamine or by traces of impurities in it.* Extrapolation to standard conditions shows that the formal potential of the system Au/complex of Au^{III} with ethylenediamine is equal to 0.24 V relative to the S.C.E. (or 0.48 ± 0.03 V relative to the normal hydrogen electrode).

When it is remembered that the potentials measured at the given concentrations, without applying a current, are equilibrium potentials, it is evident that there is an overvoltage for the reduction of the complex on the gold electrode, which is about 0.15 V at a current density of the order of $10 \mu\text{a}/\text{cm}^2$. This overvoltage increases by about 0.1 V on making the gold passive. This is clear from the fact that the reduction curves obtained on going from positive to negative potentials do not coincide with the curves obtained on going in the reverse direction. Hysteresis is observed up to the limiting diffusion current area. Passivation should be particularly high starting at a potential of 0.8 V relative to the hydrogen electrode in the same solution, or 0.3 V relative to the S.C.E. at pH 4.4, when adsorption of hydrogen on gold starts [17]. This presumably should explain the fact we have noted that the anodic dissolution of the gold electrode, which should, according to the results given above, be observed in our solutions, starting from $\varphi = 0.5$ V relative to the S.C.E., hardly occurs at all in fact.

Platinum electrode. The polarograms obtained on a platinum rotating disc electrode for the reduction of the trivalent gold complex with ethylenediamine, in a supporting electrolyte of 0.5 M ethylenediamine tartrate, have the same shape as those obtained on a gold electrode.

The volume of solution used for taking polarograms with the platinum electrode was about 90 ml.

The reproducibility of the polarographic waves obtained on using a platinum electrode is significantly worse; in this case it is necessary to control the range of potentials used for the analysis more strictly [17]. The half-wave

* When a solution of Au^{III} + ethylenediamine tartrate is in prolonged contact (more than 24 h) with metallic gold, a violet deposit of metallic gold appears on the solid surfaces.

potential for the reduction of the complex was found to be about -0.1 V relative to the S.C.E.; this almost coincides with the half-wave potential found in the case of the gold electrode. This coincidence can be explained by the gilding of the electrode which is observed when the limiting currents are measured over a sufficiently long time. In contrast to the gold electrode, in the case of the platinum electrode, the gold is deposited in the form of a smooth layer which changes during a prolonged electrolysis time from a greenish-violet color to yellow.

The relation between the limiting diffusion currents and $\sqrt{\omega}$ is also linear for the platinum electrode. The rotational speed of the electrode was varied from 1000 to 10,000 rpm. A proportionality was observed between gold concentration and the density of the limiting diffusion current over the 10^{-4} to $3 \cdot 10^{-4}$ M trivalent gold concentration range measured.

The drawback of the platinum electrode is the higher supporting electrolyte current at the potentials of the limiting diffusion current of the trivalent gold complex; it reaches $50 \mu\text{a}/\text{cm}^2$ at $\varphi = -0.2$ V relative to the S.C.E. and changes with the gold concentration of the solution. The supporting electrolyte current was determined in this instance by Pleskov's method [18], by extrapolating the values obtained for the limiting diffusion currents at the given potential to zero rotational speed of the electrode.

It is best to determine gold concentrations on a gold electrode, or to gild a platinum electrode for a long time before it is used.

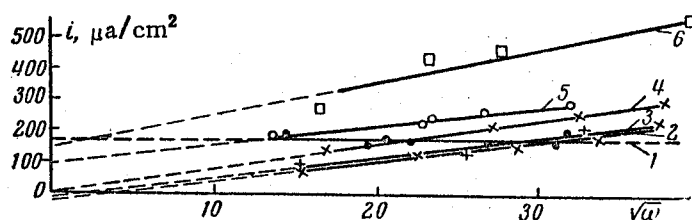


Fig. 5. Curves relating i_{limit} of the Au^{III} complex and $\sqrt{\omega}$ on taking polarograms in a small volume of solution at the following Au^{III} concentrations: 1) Supporting electrolyte; 2) $6 \cdot 10^{-7}$ M; 3) $1 \cdot 10^{-6}$ M; 4) $1 \cdot 10^{-5}$ M; 5) $1.7 \cdot 10^{-5}$ M; 6) $5 \cdot 10^{-5}$ M.

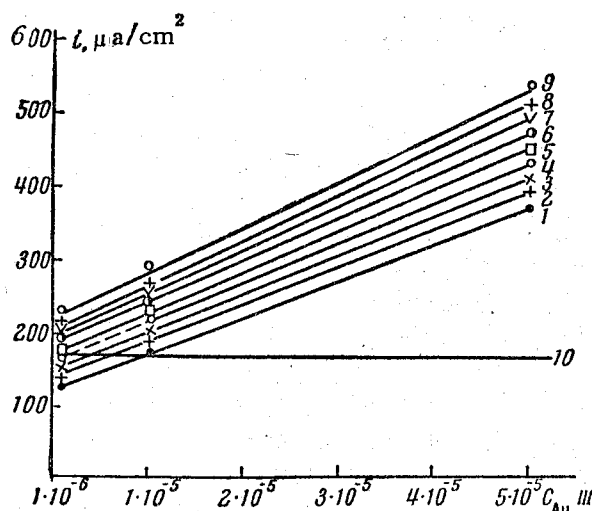


Fig. 6. Curves relating i_{limit} and concentration at the following $\sqrt{\omega}$ values: 1) 22; 2) 24; 3) 26; 4) 28; 5) 30; 6) 32; 7) 34; 8) 36; 9) 38; 10) supporting electrolyte.

Gilded platinum electrode. Three-five ml cell. To establish the possibility of determining small, absolute amounts of gold on a platinum electrode, we tried to take polarograms with a disc electrode in a small volume of solution — in a cell capable of holding 3-5 ml of solution. The size of the disc electrode ($S = 0.126 \text{ cm}^2$) and its external cover of teflon ($S_{\text{disc}} = 0.5 \text{ cm}^2$) were the same as before. The platinum electrode was gilded beforehand at $\varphi = -0.2 \text{ V}$ relative to the S.C.E for three hours in a $10^{-4} \text{ M Au}^{\text{III}}$ solution in 0.5 M ethylenediamine tartrate.

The solutions were prepared by evaporating in air an aliquot of the original concentrated solution of chloroauric acid, and dissolving the residue in the requisite amount of 0.5 M ethylenediamine tartrate.

Experiments showed that for solutions with a concentration of $7 \cdot 10^{-7}$ to $5 \cdot 10^{-5} \text{ M Au}^{\text{III}}$, there is a linear relationship between the limiting currents at $\varphi = -0.2 \text{ V}$ and $\sqrt{\omega}$ (Fig. 5), and also between the limiting currents and the concentration of the gold in solution (Fig. 6).

In contrast, in experiments with a large volume of solution in the experiments considered, a large supporting electrolyte current was observed (3-4 times greater than that observed on a gilded platinum electrode and a large volume of solution). This limits the possibility of using a platinum electrode for determining low gold concentrations. It follows from Fig. 6 that at rotational speeds of the electrode $m \geq 4600 \text{ rpm}$ ($\sqrt{\omega} \geq 22$) the lowest concentrations of gold that can be determined is 10^{-5} M , while for determining 10^{-6} M concentrations of gold it is necessary to work at $\geq 8000 \text{ rpm}$ ($\sqrt{\omega} \geq 30$). In the last instance about $1 \mu\text{g}$ of gold can be determined in a volume of 3-5 ml with an error of 10%. The sensitivity of the method increases when a gold electrode is used. A rotating electrode operating under turbulent conditions is most suitable for determining low concentrations.

We should like to thank B. N. Kabanov for discussing the results of the work.

SUMMARY

A reduction wave for the complex of gold with ethylenediamine tartrate to metallic gold is observed on gold and also on platinum electrodes, in a solution of Au^{III} in 0.5 M ethylenediamine tartrate. The half-wave potential lies at about -0.1 V relative to the saturated calomel electrode for $10^{-6} - 10^{-4} \text{ M}$ solutions of gold, and, at a current density of 10^{-5} A/cm^2 , differs by -0.15 V from the equilibrium potential in the same solution.

There is a linear relationship between the limiting current of Au^{III} and $\sqrt{\omega}$, and between the limiting current and Au^{III} concentration at constant ω values. The diffusion coefficient of the reduced complex in 0.5 M ethylenediamine tartrate has been found to be $0.7 \cdot 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$, in agreement with published results.

It has been shown that it is possible to determine trivalent gold in 0.5 M ethylenediamine tartrate on gold and platinum rotating disc electrodes, on the basis of the limiting diffusion currents at $\varphi = -0.2$ relative to the saturated calomel electrode. The lowest concentration of gold that can be determined is $10^{-6} \text{ M Au}^{\text{III}}$.

The possibility has been established of determining down to $1 \mu\text{g}$ of gold on a rotating disc electrode, using a 3-5 ml cell.

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