

THE STUDY OF THE INTERACTION BETWEEN GOLD (III) AND
2-(3-AZEPAN-1-YL)-2-HYDROXYPROPYLTHIOACETIC ACID
BY MEANS OF POTENTIOMETRIC AND AMPEROMETRIC
TITRATION METHODSH. H. DARBINYAN ^{1*}, A. S. GALSTYAN ^{2**}, H. G. KHACHATRYAN ^{1***}¹ Chair of Inorganic and Analytical Chemistry, YSU, Armenia² Chair of Organic Chemistry, YSU, Armenia

The interaction of gold (III) with 2-(3-azepan-1-yl)-2-hydroxypropylthioacetic acid has been studied by means of potentiometric titration and amperometric titration methods. It has been shown that the given interaction possesses an oxidation-reduction character with further complex formation. The ratio of interacting substances (oxidizer : reducing agent) is 1:1. A possible scheme of interaction has been also suggested.

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Keywords: potentiometric titration method, amperometric titration method.

Introduction. Preliminary concentration is necessary for the determination of gold (III) micro-quantities. Co-precipitation of the gold with metallic tellurium, which forms when adding tin(II) chloride to Te(IV) solution was proposed for this goal. The precipitate contains noble metals (Pt, Pd, Rh, Ag) as well [1]. It was also proposed to carry out the concentration process of Au, Pt, Pd and Te trace amounts using a new carbon powder containing a sulfhydryl group. The determination was supposed to be carried out by means of the atomic-emission method.

The detection limits for above-mentioned elements are 0.01%, 0.03%, 0.03% and 0.005% correspondingly [2].

Currently, the interaction of metal cations (particularly Au³⁺) with sulfur-containing reagents is of great interest. The forming coordination compounds of gold (III) may be used to obtain metallic gold nanoparticles, which, in turn, can be applied in biochemical sensors, catalysts, and medical preparations. In the work [3] an interaction between dichromate-ions and the reagent proposed by us is described. Optimal reaction conditions were revealed, as well as the range, where the amperometry main low deals, was determined, and a possible scheme of the reaction was suggested.

In the present work, the interaction between 2-(3-azepan-1-yl)-2-hydroxypropylthioacetic acid and gold (III) has been studied.

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Experimental Part. A standard solution of gold (III) (HAuCl_4) was prepared by dissolving a metallic gold (99.99%) hitch under slow heating in “aqua regia”. The denitration was realized by using a hydrochloric acid solution. The solution of 2-(3-azepan-1-yl)-2-hydroxypropylthioacetic acid (R) was prepared by dissolving a reagent exact hitch in distilled water. The solutions of the R are stable for 2–3 months. The solutions of sulfuric and hydrochloric acids of needed concentration were prepared by diluting “pure for analysis” grade concentrated solutions.

Potentiometric titration was carried out on a pH-Meter HI-2210 HANNA potentiometer equipped with a platinum electrode. Amperometric titration was realized using self-constructed amperometric station: indicator electrode – platinum wire (5 mm length), comparison electrode – mercury iodide ($E = + 0.02$ V).

A preliminary study of the interaction between gold (III) and R was carried out using qualitative reactions, which showed that firstly yellowish precipitate is formed, which is easily dissolved in reagent surplus, resulting in a transparent colorless solution.

Being a strong oxidizer [$E^0(\text{Au}^{3+}/\text{Au}^+) = 1.41$ V], gold (III), when acting with R , undergo the reduction to gold (I), which further takes part in the complex formation reaction. During the standing of the obtained solution at room temperature metallic gold layer (“gold mirror”) is formed. More deep reduction produces violet-colored precipitate – Au^{3+} is reduced to Au^0 .

Potentiometric titration was carried out within a large range of acidity – from pH 3.2 up to 0.1–6.0 mol/L by sulfuric and hydrochloric acids. All curves of potentiometric titration are similar (Fig. 1). It is evident from Fig. 1, that “potential-jump” in its classical form does not take place, although some growth takes place at the beginning of the titration, and we explain it by the formation of gold (I). The growth of the potential values corresponds to the molar ratio $\text{Au(III)} : R = 1:1$.

After that, the system potential subsides, but not spasmodically (from 960 mV to 940 mV), and this fact may be explained by a further complex formation process.

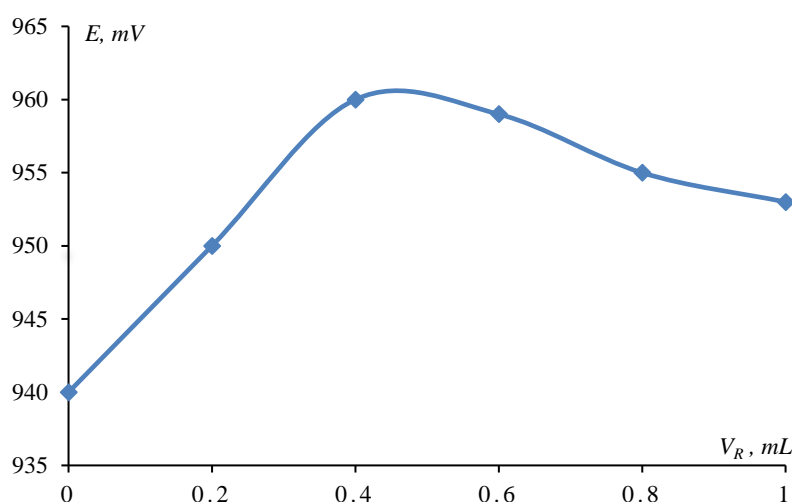


Fig. 1. Potentiometric titration curve $V_{\text{Au(III)}} = 0.5$ mL; $[\text{Au(III)}] = 9.14 \cdot 10^{-3}$ mol/L; $[R] = 1.0 \cdot 10^{-2}$ mol/L; $[\text{HCl}] = 1.0$ mol/L.

Volt-amper curves of the reacting components are obtained on sulfuric and hydrochloric acids backgrounds to choose the value of the potential for amperometric titration. The synthesized reagent undergo anode oxidation at potentials higher than 1.2 V, and gold (III) gives cathode reducing wave, starting 0.0 V. It is remarkable that anodic titration of gold (III) may be realized only on the sulfuric acid background due to the concurrent reaction of the chloride ions oxidation.

The curves of amperometric titration within cathode and anode regions are presented in Figs. 2 and 3, correspondingly. On Fig. 3 the primary growth of the diffusion current is caused by the formation of gold (I), which demonstrates electrode activity, oxidizing at the anode. A further growth of the current strength corresponds to the reagent surplus. The overkill on the curves is registered at a molar ratio of the acting components 1:1, which endorses the potentiometric determination.

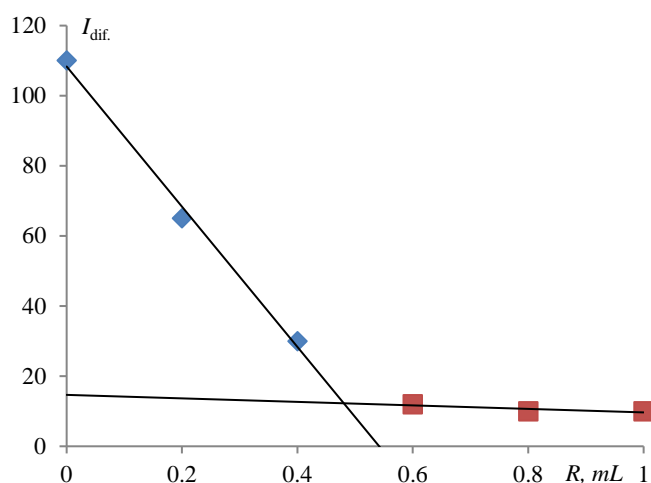


Fig. 2. Amperometric titration curve:

$V_{\text{Au(III)}} = 0.5 \text{ mL};$
 $[\text{Au(III)}] = 9.14 \cdot 10^{-3} \text{ mol/L};$
 $[\text{R}] = 2 \cdot 10^{-2} \text{ mol/L};$
 $[\text{HCl}] = 3.0 \text{ mol/L};$
 $E = +0.2 \text{ V}.$

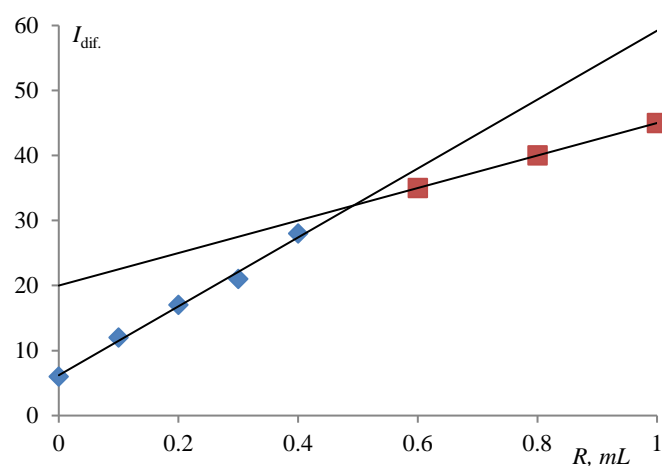
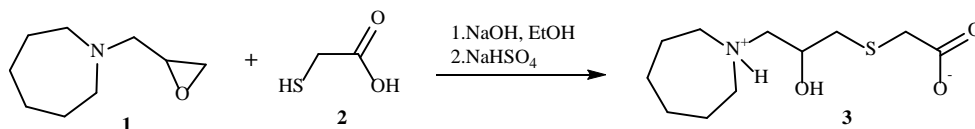


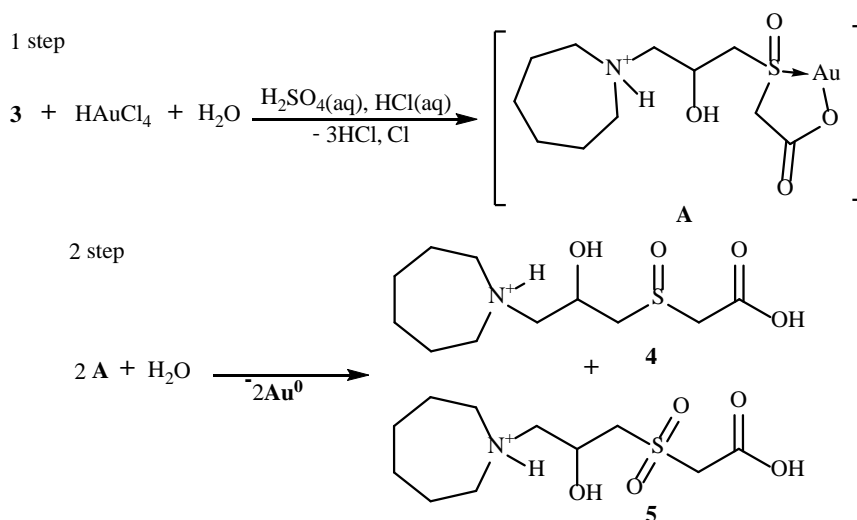
Fig. 3. Amperometric titration curve:

$V_{\text{Au(III)}} = 0.5 \text{ mL};$
 $[\text{Au(III)}] = 9.14 \cdot 10^{-3} \text{ mol/L};$
 $[\text{R}] = 2 \cdot 10^{-2} \text{ mol/L};$
 $[\text{H}_2\text{SO}_4] = 3.0 \text{ mol/L};$
 $E = +1.4 \text{ V}.$

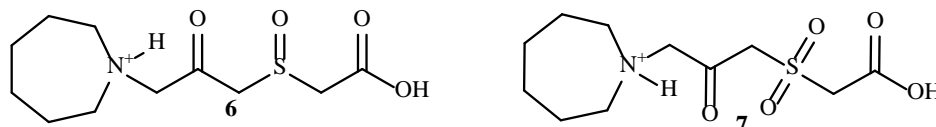
So, one can present the synthesis of R and its interaction with gold (III) as following:



Scheme 1. The synthesis of 2-(3-azepan-1-ium-1-yl)-2-hydroxypropylthioacetate (3).



Scheme 2. Two steps of gold reduction with 2-(3-azepan-1-ium-1-yl)-2-hydroxypropylthioacetate.



Scheme 3. Possible oxidation products.

¹H NMR spectra were recorded on a Varian Mercury-300 MHz in DMSO-CCl₄ mixture (1:3). Chemical shifts (δ) in ppm are reported as quoted relative to the residual signals of DMSO-*d*₆ (2.5 for ¹H NMR) as internal references. The coupling constants (*J*) are given in hertz. All reagents were of reagent grade and used as such or distilled prior to use. The starting 1-(oxiran-2-ylmethyl)azepane was prepared as previously reported [4].

2-(3-(Azepan-1-ium-1-yl)-2-hydroxypropyl)thioacetate (3). To a mixture of 3.22 g (35 mmol) of 2-mercaptoacetic acid in 30 mL of ethanol is added 1.8 g (45 mmol) of sodium hydroxide, 5.43 g (35 mmol) of 1-(oxiran-2-ylmethyl)azepane and the whole is stirred for 1 h at room temperature and 5 h at 40°C. The mixture is cooled, 5.4 g (45 mmol) NaHSO₄ and 3 mL water are added, and the whole is stirred for 12 h at room temperature. After the mixture is filtered off, washed with ethanol, the solvent is removed in a vacuum and diethyl ether is added. The precipitated crystals are filtered off, washed with diethyl ether and dried.

Yield 65%, m.p.143–144°C. $^1\text{H NMR}$ (300 MHz, DMSO), δ , ppm: 6.24 br.s (2H, HN^+ , OH); 3.81 ddd ($J = 11.9, 7.1, 5.1 \text{ Hz}$, 1H, CHOH); 3.16 d ($J = 1.2 \text{ Hz}$, 2H, $\text{SCH}_2\text{C}=\text{O}$), 2.92–2.80 m (4H, NCH_2 in cycle); 2.78–2.65 m (2H, NCH_2), 2.65–2.53 m (2H, CH_2S); 1.79–1.53 m (8H, $(\text{CH}_2)_4$ in cycle).

Found, %: C, 53.22; H, 8.45; N, 5.88; S, 13.09. $\text{C}_{11}\text{H}_{21}\text{NO}_3\text{S}$. Calculated, %: C, 53.41; H, 8.56; N, 5.66; S, 12.96.

Conclusion. Gold (III), acting with R, is reduced to gold (I), and after that, for several hours, continues to be reduced to metallic gold. The system 2-(3-azepan-1-yl)-2-hydroxypropylthioacetic acid – gold (III) has been studied by means of potentiometric titration and amperometric titration and the results proved that the oxidizer : reducing agent ratio is 1:1.

A possible scheme of the reaction has been suggested.

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ՈՍԿԻ (III)-Ի ԵՎ 2-(3-ԱՉԵՊԱՆ-1-ԻԼ)-2-
ՀԻԴՐՕՔՍԻՊԻԼԹԻՆՈՒԹՅԱԽԱԹՎԻ ՓՈԽԱՉԳԵՑՈՒԹՅԱՆ
ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ ՊՈՏԵՆՑԻԱԼԱԶՈՒՓԱԿԱՆ ԵՎ
ԱՄՊԵՐՈՒՄՆԱՍԻՐՈՒԹՅԱՆ ՏԻՏՐՄԱՆ ԵՂԱՆԱԿՆԵՐՈՎ

Ոսկի (III)-ի և 2-(3-ազեպան-1-իլ)-2-հիդրօքսիպրոպիլթիօպրագախաթթվի միջև փոխազդեցությունն ուսումնասիրվել է պոտենցիալաչափական և ամպերաչափական տիտրման եղանակների միջոցով: Ապացուցվել է, որ տվյալ փոխազդեցությունն ունի վերօքս բնույթ հետագա կոմպլեքսազոյացմամբ: Փոխազդող նյութերի (օքսիդիչ : վերականգնիչ) մոլային հարաբերակցությունը 1:1 է: Առաջարկվել է նաև փոխազդեցության հավանական ուրվագիրը:

Г. Г. ДАРБИНЯН, А. С. ГАЛСТЯН, А. Г. ХАЧАТРЯН

ИЗУЧЕНИЕ ВЗАИМОДЕЙСТВИЯ МЕЖДУ ЗОЛОТОМ (III) И
2-(3-АЗЕПАН-1-ИЛ)-2-ГИДРОКСИПРОПИЛТИОУКСУСНОЙ КИСЛОТОЙ
МЕТОДАМИ ПОТЕНЦИОМЕТРИЧЕСКОГО И
АМПЕРОМЕТРИЧЕСКОГО ТИТРОВАНИЯ

Взаимодействие между золотом (III) и 2-(3-азепан-1-ил)-2-гидрокси-пропилтиоуксусной кислотой изучено методами потенциометрического и амперометрического титрования. Показано, что данное взаимодействие имеет окислительно-восстановительный характер с последующим комплексообразованием. Мольное соотношение реагирующих веществ (окислитель : восстановитель) равно 1:1. Предложена также возможная схема взаимодействия.