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Anodic corrosion of gold in solutions of diaminoalkanes

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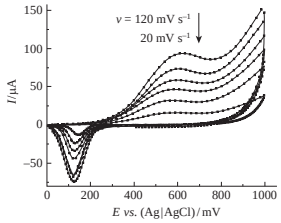
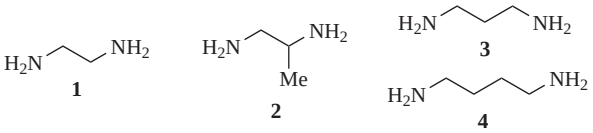
The anodic corrosion of gold followed by its deposition on the cathode as a compact precipitate occurs upon electrolysis of weakly alkaline aqueous solutions of diaminoalkanes, among which 1,2-diaminoethane proved to be the most effective. The process has been characterized by cyclic voltammetry.



Metallic gold is substantially stable to chemical and electrochemical impacts. Gold is extracted from minerals *via* dissolution in potassium cyanide solutions. The search for safer techniques for the extraction of gold from minerals, including electrochemical methods, has been in progress for many years.[1,2] The electrochemical behavior of gold is of great theoretical and practical interest.[3] Gold can undergo corrosion under anodic polarization conditions.[4,5] Anodic dissolution of a gold electrode can occur in perchloric or sulfuric acid solutions containing chloride or bromide ions.[6–8] Thiourea promotes anodic dissolution of gold at potentials (E) of 0.45–0.65 V *via* one-electron process.[9,10] The anodic dissolution of Au in an alkaline solution of thiosulfate has been studied by cyclic voltammetry and coulometry.[11] The regularities of gold dissolution in alkaline sulfite thiourea electrolytes have been investigated by microgravimetry and cyclic voltammetry[12] assuming the formation of sulfite complexes of gold.[13]

Electrochemical characteristics of gold electrode have also been studied in solutions of various organic compounds capable of complex formation. For example, the anodic dissolution of gold was found during recording of cyclic voltammograms (CVs) of 3-mercaptopropionic and *meso*-2,3-dimethylsuccinic acids in $LiClO_4$ solutions.[14] In the absence of these compounds, oxidation of gold proceeds at potentials higher than 0.8 V, while their addition resulted in the broadening of the potential range to 0.5–0.8 V. Influence of amino acids on gold electrode corrosion was also indicated.[15–17] The anodic corrosion of a gold electrode in solutions of amino compounds, 1,5-diazabicyclo[3.1.0]hexanes (DABH) and 1,3-diaminopropane,[18–20] was accompanied by the formation of complexes, which passed into the solution and were reduced at the cathode to give a compact precipitate of metallic gold. 1,3-Diaminopropane induced gold corrosion more easily than DABH (the anodic peak in the CV was shifted by 0.3–0.5 V toward negative potentials with respect to that for DABH) since 1,3-diaminopropane would form complexes more readily as compared to DABH.

In this study, we extended the number of compounds capable of forming complexes with gold cations and active in gold anodic dissolution processes. For this purpose, other diaminoalkanes such as 1,2-diaminoethane **1**, 1,2-diaminopropane **2**, 1,4-diaminobutane **4**, along with previously studied 1,3-diaminopropane **3**, were tested. To elucidate the possible mechanism of anodic corrosion of gold in weakly alkaline solutions of these diamines, cyclic voltammetry with a slow potential scan rate (1 mV s^{-1}) was used, and computer separation of unresolved peaks was applied for analysis of the obtained CVs.‡



Initially, in CVs for a gold anode in 0.1 M aqueous solutions of model 1,2-diaminoethane **1** recorded in the potential range of 0–1000 mV, both anodic and cathodic responses were observed only in the first cycle. No responses were detected after the second and subsequent cycles, evidently due to strong adsorption of ligand **1** on the anode due to complex formation which passivated the anode surface. Well reproducible CV could be obtained only when this electrode was maintained at E = 2.5 V for 2 min after every cycle. After 10–20 cycles, a gold film was formed on the cathode surface. The CV recorded at different potential scan rates in the range E = 0–1000 mV are shown in

† Deceased in 2017.

‡ 1,2-Diaminoethane **1**, 1,2-diaminopropane **2**, 1,3-diaminopropane **3**, and 1,4-diaminobutane **4** were purchased from Acros Organics and used without further purification. All electrochemical measurements were carried out in an undivided three electrode 50 ml cell. A 0.3 cm long Au wire (99.99%) with a diameter of 0.3 mm soldered in glass was used as the stationary working electrode. A Pt wire of the same size soldered in glass served as the auxiliary electrode and a silver chloride electrode (Ag/AgCl/3MKCl) was used as the reference electrode. The supporting electrolyte was a solution of K_2CO_3 (0.05 mol dm^{-3}) in doubly distilled water (pH 11.1). The pH value was measured on a pH-150 MI instrument using a glass electrode. A solution of K_2CO_3 (10 ml) was poured into the cell and 1 mmol of the corresponding amine was added dropwise to reach its concentration of 0.1 mol dm^{-3}. The cell was incubated at 25±0.1 °C. Before recording CV curves, a solution was purged with argon for 20 min. Cyclic voltammetry was performed on a computerized IPC-Compact potentiostat, the CVs were recorded at different potential scan rates in the range E = 0–1000 mV, for each solution the curves were recorded at least three times.

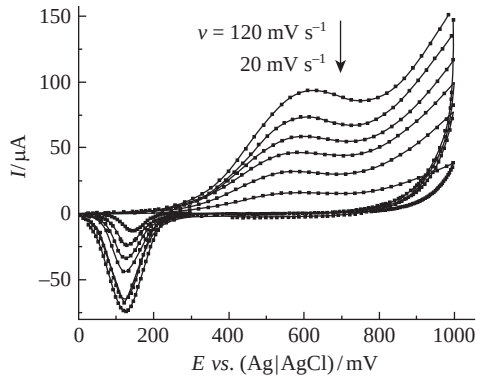


Figure 1 The CVs of gold anode in 0.1 M solution of 1,2-diaminoethane **1** in 0.05 M solution of K_2CO_3. The potential scan rates are 20 40, 60, 80, 100 and 120 mV s^{-1}.

Figure 1. Clear peaks in the potential range E = 500–600 mV appear in the anodic branches of the CV. For exact determination of the maximum peak of the anodic current ($I_{p,a}$) and for calculation of their areas, the CV anodic branches were presented as sums of the background and faradaic currents. The faradaic current peak was represented by a Gaussian function.

The dependences of the background and faradaic currents on the potential at all studied scan rates were found by optimization of the Gaussian function parameters. The optimal parameters were calculated using the Original-61 software. According to the calculations affording the maximum currents ($I_{p,a}$) and charges (Q), the $I_{p,a}$ values increased with increasing potential scan rate v (Figure 2). Evidently, gold corrosion occurs together with pronounced adsorption of 1,2-diamonoethane **1** on the anode surface, the electron transfer being the rate-limiting step.

Upon reversal of the potential scan, the peaks in the cathodic branches appeared in the potential range 80–150 mV. This result indicates that the gold complexes with ligand **1** are reduced at the cathode. It can be assumed that in this case as well as in the case of anodic polarization, the reduction of gold complexes occurred directly on the cathode surface, with the electron transfer being the rate-limiting step. In the above cases, the Laviron equation[21] could be applied [equation (1)].

$$I_p = nFQv/4RT, \quad (1)$$

where I_p is the maximum peak of the current, n is the number of electrons participating in the reaction with one molecule of ligand **1**, F is the Faraday constant (96485 C mol^{-1}), Q is the charge corresponding to the peak area in the cathodic branch of the CV, v is the potential scan rate (mV s^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature.

Using the Laviron equation, the number of electrons (n) participating in the reaction for the cathodic process was found to be 0.89–1.12 for v = 20–120 mV s^{-1}, indicating that only one electron participates in the cathodic reduction of the Au complex with ligand **1**. The calculated n values for the anodic process were found to be 0.5 for all of the potential scan rates. Evidently, the stoichiometry of the anodic process cannot be established by the direct method. Probably, the anodic process is multi-electronic one, every anodic peak in the CV in solutions of ligand **1** being the sum of peaks that refer to separate electron transfer processes. If both the anodic and cathodic processes occur with gold electrode surface completely covered with ligand **1**, the stoichiometry of the anodic process can be calculated *via* the ratio between the charges consumed in these processes. It was found that this ratio was 2.85–3.08, depending on the potential scan rate, *i.e.*, if only one electron participates in the cathodic process, then three electrons take part in the anodic one.

The assumption that the anodic peaks of the CV in solutions of ligand **1** correspond to a complex was confirmed by recording the CV at low potential scan rate (1 mV s^{-1}). Two peaks, at 340 and 510 mV, were clearly seen in the anodic branch, the peak area at 340 mV being twice less than that at 510 mV (Figure 3) according to description using the Gaussian function. This result indicates that electron transfer in the anodic process was stepwise (first, one electron and then, two electrons) resulting in two different complexes. The data obtained allow us to assume that the cathodic reduction of the anodic oxidation products corresponded to the conversion of divalent Au complex into a univalent state followed by its reduction into a compact precipitate of metallic gold. However, this process needs additional investigations.

The CV obtained for a solution of 1,2-diaminopropane **2** as well as the anodic peaks of CV of gold electrode in 0.1 M solution of this ligand (0.05 M solution of K_2CO_3 as a supporting electrolyte), presented as the Gaussian functions, proved to be similar to those obtained for ligand **1** (Figures S1, S2, see Online Supplementary Materials). In this case, like in the electrolysis in a solution of ligand **1**, the cleaning of the anode was necessary after every cycle, which was accomplished by maintaining the anode at E = 2.5 V for 2 min. Since the number of electrons participating in the reduction of Au complexes with ligand **2** calculated using Laviron equation was 0.95–1.1, one may conclude that the cathodic reduction of the Au complex with ligand **2** in a solution of this ligand involved the transfer of one electron. In addition, the ratio of the charge consumed in the anodic process to that of the cathodic one at different potential scan rates proved to be 2.87–3.10 and the anodic peak at v = 1 mV s^{-1} was separated into two peaks with 1:2 ratio of the areas (Figure S3). Moreover, the maximum values of cathodic and anodic peaks ($I_{p,c}$ and $I_{p,a}$) found for

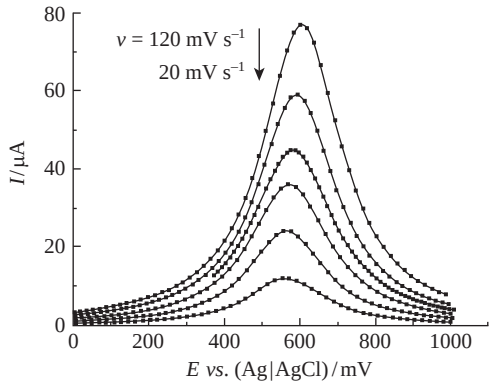


Figure 2 The anodic peaks of CV of gold electrode in 0.1 M solution of 1,2-diaminoethane **1** in 0.05 M solution of K_2CO_3, presented as the Gaussian functions. The potential scan rates are 20 40, 60, 80, 100 and 120 mV s^{-1}.

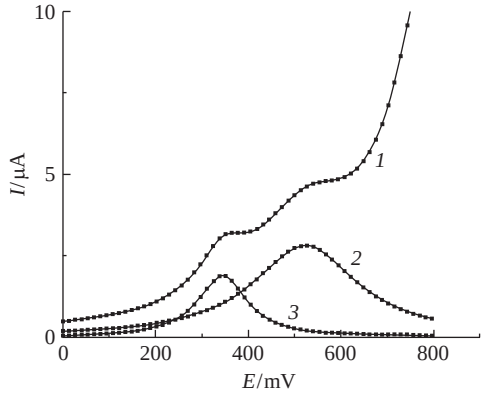


Figure 3 The anodic branch of cyclic voltammetry of Au electrode in 0.1 M solution of ligand **1** in 0.05 M solution of K_2CO_3 at the potential scan rate of 1 mV s^{-1}.

solutions of ligands **1** and **2** were linearly dependent on the potential scan rate (Figure S4).

Investigation of the behavior of the Au electrode in a solution of 1,3-diaminopropane **3** showed that the anode cleaning was not necessary for obtaining reproducible CV (Figure S5). The $I_{p,c}$ value depended linearly on the potential scan rate (Figure S4). The calculated number of electrons for the cathodic process using the Laviron equation was about 2. The anodic branch of CV obtained at v = 1 mV s^{-1} represents a sum of two peaks at 510 and 630 mV, with 1:2 ratio of the peak areas, similarly to the electrolysis in solutions of diamines **1** and **2** (Figure S6).

The behavior of the Au electrode in a solution of 1,4-diaminobutane **4** (Figures S7, S8) differed from those for diamines **1**–**3**. The $I_{p,a}$ and $I_{p,c}$ values were proportional to $v^{0.5}$. This implies that both the anodic and cathodic processes are controlled by the diffusion of ligand **4** to the Au electrode surface. The anodic peak was not separated into two peaks even at low potential scan rates.

Comparison between the Au electrode behaviors in solutions of diamines **1**–**4** shows that only 1,2-diamines **1** and **2** are strongly adsorbed on the Au electrode surface and thus completely block the surface. A linear dependence of the anodic peaks on the potential scan rate was observed only for 1,2-diamines **1** and **2**. In solutions of these diamines, one electron is involved in the cathodic process and three electrons participate in the anodic process, the later process being stepwise: one electron and then two electrons.

The behavior of the Au electrode in a solution of ligand **3** was intermediate between those for ligands **1** and **2**. Indeed, the linear dependence of the current peaks in a solution of ligand **3** was observed only for the cathodic process. No blocking of the electrode surface was detected for this ligand. The number of electrons taking part in the cathodic process proved to be 2, that correlates with the structure of previously isolated complex of 1,3-diaminopropane **3** with divalent Au cation.[20]

The CV parameters for all of the studied diaminoalkanes are given in Table 1. As can be seen, $I_{p,c}$ and $I_{p,a}$ decrease and $E_{p,a}$ increases on going from 1,2-diaminoalkanes **1** and **2** to compounds **3** and **4**. This means that the anodic corrosion of gold occurs more easily for ligand **1** and the corrosion product (Au complex of ligand **1**) is also reduced more easily at the cathode. This pattern of the change of the Au electrochemical behavior in solutions of different diaminoalkanes is associated, most likely, with an influence of structural factors, because vicinal diaminoalkanes (1,2-diaminoalkanes) are more prone to complex formation with metal cations than diaminoalkanes containing longer aliphatic linkers.[22]

In summary, the electrochemical behavior of the Au anode in weakly alkaline aqueous solutions of aliphatic diaminoalkanes (1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, and 1,4-diaminobutane) was examined by cyclic voltammetry. It was found that a common feature of the Au anode in solutions of all of these diamines is the anodic corrosion of gold followed by the transfer of gold to the cathode as a compact precipitate. Among the studied diamines, 1,2-diaminoethane, which is a readily available commercial product proved to be most efficient despite the passivating action that can be overcome by performing the process at potentials of not less than 2.5 V. Thus, particularly 1,2-diaminoethane can be recommended for further studies of the electrochemical corrosion of gold for preparative purposes.

Table 1 The CV parameters for the solutions of diaminoalkanes **1**–**4**.[a]

Diamino-alkane	Cathodic branch		Anodic branch	
	$I_{p,c}$/mA	$E_{p,c}$/mV	$I_{p,c}$/mA	$E_{p,a}$/mV
1	–74	105	63	572
2	–51	91	50	600
3	–22	110	26	680
4	–28	108	40	660

[a] $I_{p,c}$ is the maximum peak of the cathodic current, $I_{p,a}$ is the maximum peak of the anodic current, $E_{p,c}$ and $E_{p,a}$ are the corresponding potentials.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.024.

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