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Dissolution Behavior of Gold in Alkaline Media Using Thiourea

Cristian Vargas[1]*, Patricio Navarro[1], Daniel Espinoza[1], Jorge Manríquez[1], Erica Mejía[2]

[1]Departamento de Ingeniería Metalúrgica, Universidad de Santiago de Chile, Avda, Libertador Bernardo O´Higgins, Santiago, Chile
[2]Grupo de Investigación GIIAM, Facultad de Ingeniería, Institución Universitaria Pascual Bravo, Medellín, Colombia
Email: *cristian.vargas@usach.cl

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Abstract

In this work the dissolutive behavior of gold in alkaline medium using thiourea (TU), under different variables, was studied in a theoretical and experimental way, in order to determine the conditions under which it is feasible to dissolve gold in thiourea-alkaline medium. A thermodynamic study was conducted by chemical speciation using the method of Rojas-Hernández, together with an electrochemical study where the electric potential was swept in the anodic direction. The main results of the thermodynamic study were that formamidine disulfide (FDS) and sulfinic compounds (S.C.) prevail at alkaline pH; by increasing the initial concentration of thiourea at alkaline pH, the presence of the gold complex is almost zero for any initial concentration of thiourea. By including sodium sulfite in the gold-thiourea system, it was possible to obtain the Au(I)-TU complex at alkaline pH, with a presence of 95.13%. Electrochemical tests allowed verifying that in the absence of sodium sulfite the dissolution of gold in an alkaline medium is very slow but adding sodium sulfite improvements become evident in the dissolution of the metal. Therefore, sodium sulfite catalyzes the gold dissolution process and stabilizes the thiourea. With this study it was possible to establish the feasibility of using thiourea in an alkaline medium for the dissolution of gold, and the conditions under which it is possible to dissolve the gold in that medium. With these fundamentals and conditions, it is now possible to move forward to test this system for minerals and/or concentrates containing gold.

Keywords

Gold, Alkaline, Thiourea, Dissolution Behavior, Sodium Sulfite

1. Introduction

The use of thiourea ($SC(NH_2)_2$) (TU) has been studied extensively, mainly because it is not harmful to the environment, nontoxic to human beings, and the dissolution of gold in thiourea solutions is much faster than in cyanide solutions. The dissolution of gold in thiourea solutions was reported for the first time in 1941, and it was continued in 1960 [1]. It has been reported that gold dissolves more efficiently with thiourea in acid than in alkaline solution. Thiourea is unstable above pH = 4.3, and its degradation is also caused by oxidation. Thiourea is oxidized to formamidine disulfide (FDS), which is an active oxidant for dissolving gold. FDS is also oxidized to various intermediary species whose final product is elemental sulfur, which causes the passivation of precious metals, and their dissolution tends to stop [2] [3].

In the leaching of gold with acid TU solutions there are several problems, such as a greater consumption of TU during the redissolution of Au, equipment corrosion in acid solution, low selectivity of the Au leaching reaction, and complicated reagent regeneration and purification procedures. To overcome the above inconveniences, the leaching of Au with an alkaline TU solution has been proposed, and some research work has been carried out [4] [5]. Since the leaching of Au with alkaline TU solution is still in the research and development stage, it is necessary to make an adequate study of the thermodynamic aspects of the Au-TU system under different pH and ligand concentration conditions that can clarify and establish those required for the operation's success. Therefore, this paper involved chemical and electrochemical studies meant to achieve a better understanding of the gold-thiourea system in an alkaline environment, and to establish the most favorable conditions for the leaching.

2. Methodology

2.1. Chemical Speciation

The chemical speciation diagrams are constructed to show the relation of the different chemical species (thiourea and gold-thiourea) either as a function of pH or of ligand concentration and establishing their predominant behavior in solution. The construction of those diagrams in this study is based on the method of Rojas-Hernández [6] [7], which considers the formation of complexes in which a metal ion M reacts with ligand L to form the complex ML. For these reactions the formation equilibrium or stability constants are considered. The stability constants used in the construction of the diagrams are shown in **Table 1**.

2.2. Electrochemical Tests

Linear potential scans were made, from the rest potential to 1000 mV in the anodic direction, at a scanning rate of 10 mV/s. To determine the electrochemical behavior of the gold, tests were run under different pH, thiourea concentration, and additive presence and content.

The solutions used were prepared with distilled and deionized water, with analytical grade reagents.

Table 1. Stability constants of the studied system.

Metal	Ligand	Equilibrium reaction	Log K
Au(I)	TU (SC(NH$_2$)$_2$	$2SC(NH_2)_2 = [SC(NH)NH_2]_2 + 2H^+ + 2e$	−4.3
	TU (SC(NH$_2$)$_2$	$Au^+ + 2SC(NH_2)_2 = Au[SC(NH_2)_2]_2^+$	23.3

All the electrochemical tests were performed with a conventional three-electrode system consisting of a gold working electrode, a platinum wire as counter electrode, and a Ag/AgCl reference electrode.

The electrochemical measurements were made with a model PGP-201 Radiometer Potentiosat/Galvanostat controlled by the Voltamaster 4.0 software. All the potential values are referred to the standard hydrogen electrode (SHE).

3. Results and Discussion

3.1. Thiourea Speciation

Experimental evidence has been found that TU is degraded irreversibly to formamidine disulfide (FDS) and sulfinic compounds (S.C.), reaching elemental sulfur as final product. To confirm the above and determine its stability under different conditions, the speciation diagrams for this ligand were constructed. Figure 1(a) and Figure 1(b) present the speciation diagrams of TU as a function of the concentration of thiourea at alkaline pH.

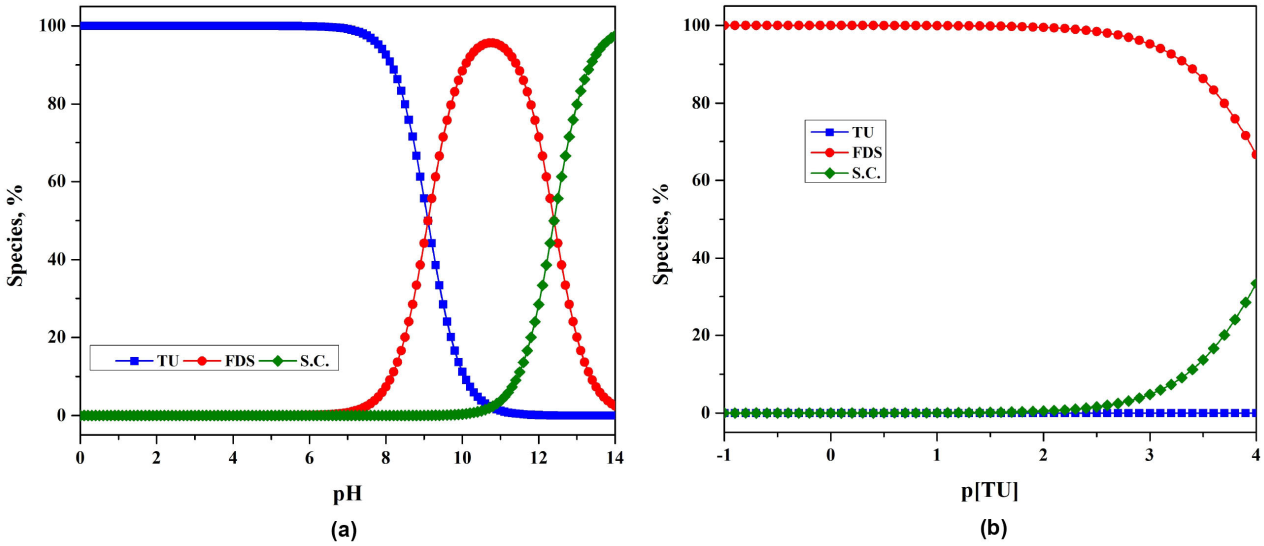
It is seen that at pH above 10 there is no more TU in the system, DSF starts degrading, and sulfinic compounds become predominant at pH greater than 12.5. In Figure 1(b) it is also seen that at alkaline pH the DSF predominates up to p[TU] = 2.3. As the initial TU concentration is reduced, the presence of DSF decreases, causing an increase of the presence the sulfinic compounds. Furthermore, it can also be confirmed that at alkaline pH there is no presence of TU in the system.

3.2. Au(I)-TU System Speciation

Gold can form only one complex with thiourea, namely $Au\left[SC\left(NH_2\right)_2\right]_2^+$. The behavior of the Au-TU system as a function of pH and of the TU concentration is shown in Figure 2(a) and Figure 2(b). The Au-TU complex predominates up to pH 8.8; from that value up to about 12.4, DSF predominates. Above pH 12.4 the presence of DSF decreases, sulfinic compounds become predominant, and the presence of the Au-TU complex is not detected in the system.

Figure 2(b) shows that at alkaline pH the presence of Au(I) and of the Au-TU complex is almost imperceptible over the whole range of p[TU], with DSF as the predominant compound from high thiourea concentrations (p[TU] = −1.0) to p[TU] = 3.3, at which point the change in predominance occurs, with sulfinic compounds starting to become preponderant at the expense of DSF.

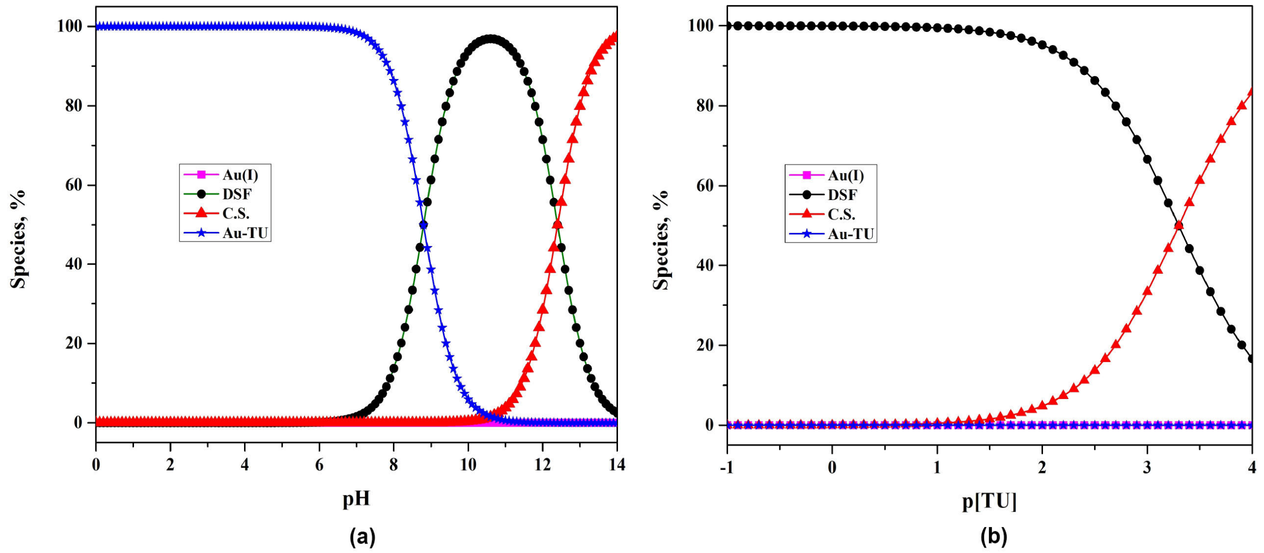
The behavior of this system in the presence of sodium sulfite was also studied. This compound stabilizes TU over the whole pH range, so it is very important in the stability of the Au-TU complex. Figure 3 shows the speciation diagrams of the Au-TU-sodium sulfite system.



(a)

(b)

Figure 1. Speciation of thiourea at 25 as a function of pH (a) and of thiourea concentration (b).



(a)

(b)

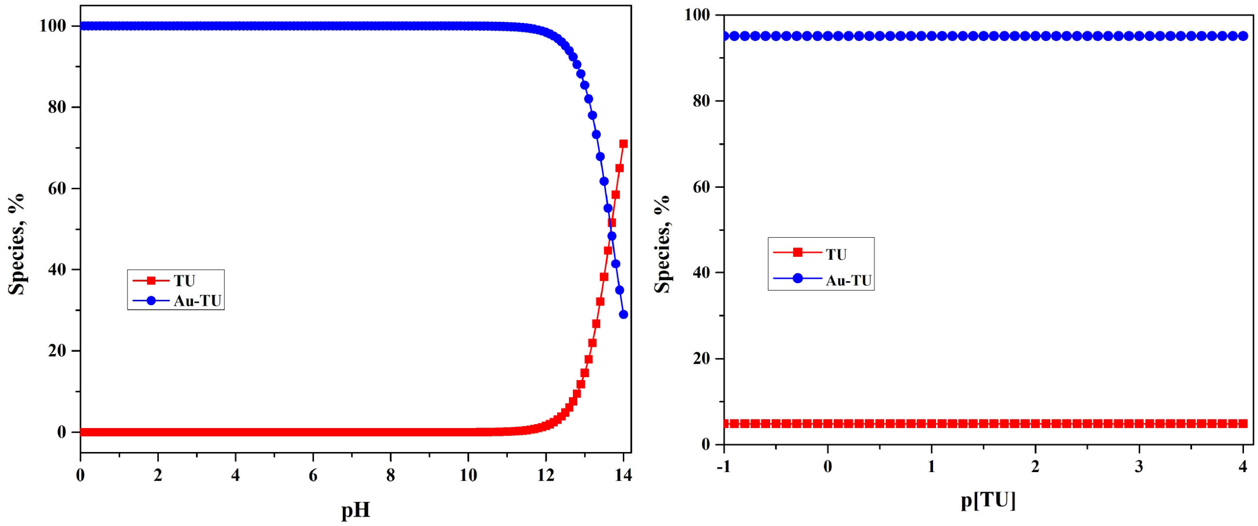
Figure 2. Speciation of the Au-TU system at 25˚C as a function of pH (a) and of TU concentration (b).

It is seen that the Au-TU complex predominates up to pH 13.7. At higher pH TU starts predominating; its presence is due to the stabilizing action of sulfite, preventing its irreversible oxidation. Figure 3(b) shows that as TU concentration increases, the predominant species is always the Au-TU complex.

3.3. Electrochemical Behavior of the Au-TU System

Figure 4(a) and Figure 4(b) present the electrochemical behavior of Au as a function of pH (0.1 M thiourea and 25˚C) and of TU concentration (pH = 12.5 and 25˚C).

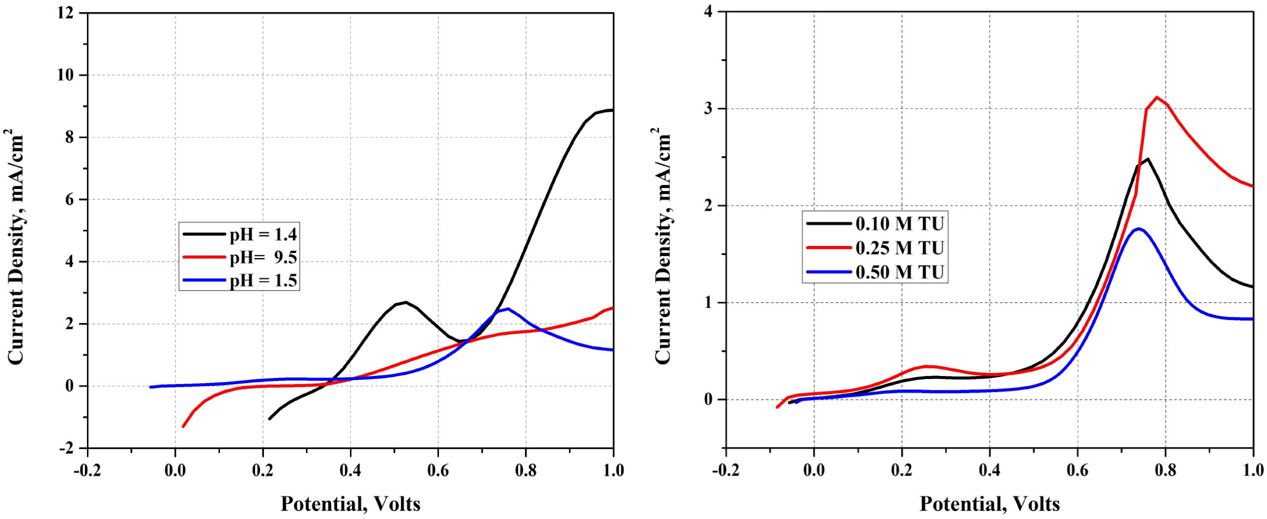
It is seen that in the Au-TU system, at acid pH (1.4) two peaks or singularities appear, pointing to the occurrence of some transformation in the system. The



(a)

(b)

Figure 3. Speciation of the Au-TU-sodium sulfite system at 25˚C as a function of pH (a) and of TU concentration (b).



(a)

(b)

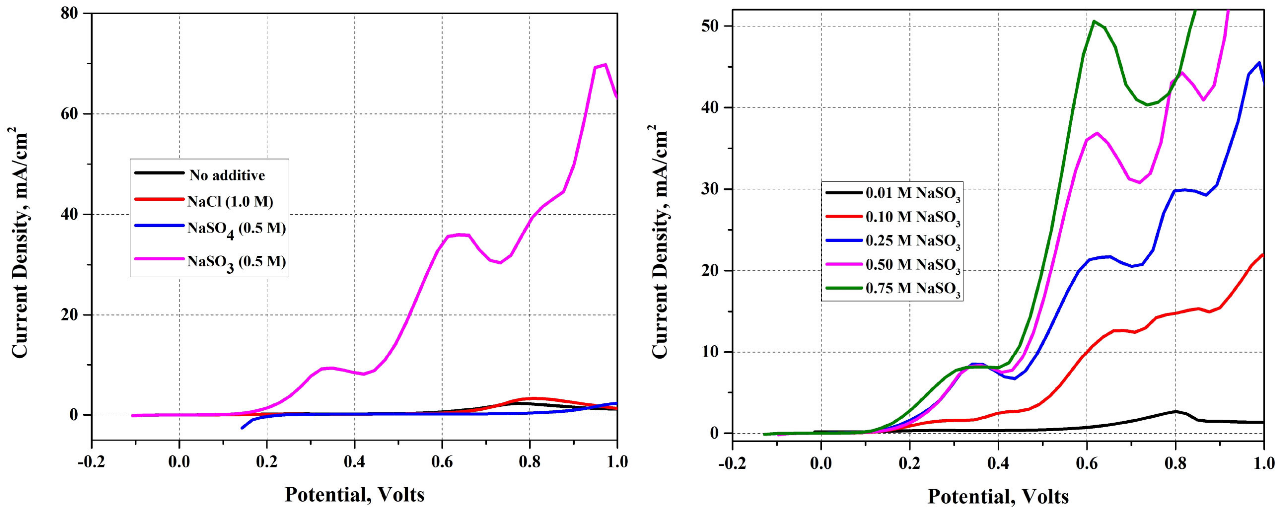
Figure 4. Linear polarization curves for a gold electrode as a function of pH (a) and of TU concentration (b).

first peak (0.52 V) would correspond to the formation of the Au-TU complex, while the second (0.95 V) would indicate the transformation of TU into DSF. These results are like those obtained by Bolzán *et al.* [8] and Yang *et al.* [9], who proposed the occurrence of the following reactions.

$$\mathrm{Au} + 2\mathrm{SC}\left(\mathrm{NH_2}\right)_2 \Leftrightarrow \mathrm{Au}\left[\mathrm{SC}\left(\mathrm{NH_2}\right)_2\right]_2^+ + \mathrm{e},\ \ \mathrm{E}^\circ = 0.38\ \mathrm{V_{NHE}} \qquad (1)$$

$$2\mathrm{SC}\left(\mathrm{NH_2}\right)_2 \Leftrightarrow \mathrm{NH_2}\left(\mathrm{NH}\right)\mathrm{CSSC}\left(\mathrm{NH}\right)\mathrm{NH_2} + 2\,\mathrm{H^+} + 2\mathrm{e},\ \ \mathrm{E}^\circ = 0.42\ \mathrm{V_{NHE}} \qquad (2)$$

At pH 9.5 no singularity is seen, but not so at pH 12.5, when the peak of the DSF formation reaction (0.76 V) appears. Furthermore, a greater electrochemical activity under acid conditions (pH = 1.4) is seen than at more alkaline pH



(a)

(b)

Figure 5. Linear polarization curves for a gold electrode in the presence of different additives (a), and of the concentration of sodium sulfite (b).

(9.5 and 12.5), and at pH 12.5 it is not possible to see the typical singularity that indicates the formation of the Au-TU complex, confirming what had been shown previously for chemical speciation. Comparing the curves shown in **Figure 4(b)**, it is seen that for all the TU concentrations that were studied, the singularities occur at similar potentials, so the variation of the TU concentration at pH 12.5 has no influence on the potential at which the system's chemical transformations occur.

The effect of the presence of additives on the electrochemical behavior of gold in an alkaline medium with thiourea was also determined. **Figure 5(a)** shows that the presence of sodium sulfite increases visibly the electrochemical activity of gold compared to the other solutions that were studied. Therefore, sodium sulfite allows obtaining the Au-TU complex defining an important condition in the use of thiourea for leaching gold in an alkaline medium. **Figure 5(b)** shows that the dissolution of gold increases as the presence of sodium sulfite also increases.

4. Conclusions

The speciation studies made allowed establishing that regardless of the TU concentration and in an alkaline medium, the TU is not predominant in the system because it decomposes irreversibly until it forms sulfinic compounds. This means that there is no thiourea available for complexing the gold, and that is why under alkaline conditions and for any TU concentration it is not possible to obtain the Au-TU complex as the predominant species. However, the addition of sodium sulfite stabilizes the thiourea, allowing the predominance of the Au-TU complex in an alkaline medium.

The electrochemical studies showed different current peaks at given potential values, which represent the transformations undergone by the species present in the system. In an alkaline medium there was no evidence of the formation of the Au-TU complex. The concentration of thiourea does not affect the potential at which the singularities occur, however, a greater TU concentration does not imply a higher rate of dissolution. The addition of sodium sulfite to the thiourea solution showed clearly the formation peak of the Au-TU complex, greatly increasing the anodic current of the gold electrode, speeding up its dissolution.

The results obtained allow establishing certain conditions of use of thiourea in alkaline medium to dissolve gold. The application of this system for minerals and/or concentrates required additional study regarding the effect and interaction of some impurities, as well as the determination of kinetic mechanisms and parameters of interest for a better understanding and optimization of the process.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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