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Electrochemical studies on gold electrodes in acidic solutions of thiourea containing gold (I) thiourea complex ions

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Electrochemical studies were made of the behaviour of gold electrodes in degassed acidic solutions containing between 0·001 to 0·03 M thiourea and between 10^{-5} to 10^{-3} M gold(I)thiourea. At anodic overpotentials of up to 0·3 V the dissolution of gold was rapid, and nearly reached the maximum diffusion-controlled rate. The exchange current density was greater than 10^{-6} A cm^{-2}, and dissolution proceeded at 100% efficiency. At higher anodic potentials, thiourea was oxidized to formamidine disulphide and other sulphur-containing compounds and the dissolution of gold became partly inhibited, while the current efficiency decreased markedly.

The reduction of gold(I)thiourea was diffusion-controlled at cathodic overpotentials between −0·15 to −0·35 V, after which slight inhibition was observed. Thiourea itself did not contribute to the cathodic reaction, but formamidine disulphide could be reduced on a freshly deposited gold surface; in the absence of gold(I)thiourea in the solution, the reduction of formamidine disulphide caused rapid passivation of the gold surface. In 0·01 M thiourea and 0·1 M sulphuric or perchloric acid, the diffusion coefficient of the $Au(CS(NH_2)_2)_2^+$ ion was $1{\cdot}1 \times 10^{-5}$ cm^2 s^{-1} at 30°C.

The standard reduction potential at 30°C of the redox couple $Au(CS(NH_2)_2)_2^+ | Au$ on a fresh gold surface was $E_0 = 0{\cdot}352$ V, but on a passivated gold surface this value increased to as much as $E_0 = 0{\cdot}41$ V.

1. Introduction

The dissolution of gold in acidic solutions of thiourea was reported in 1941 by Plaksin [1]. Preisler [2] also observed this phenomenon, but did not report it until some years later [3]. The possible hydrometallurgical applications of this reaction have resulted in further investigations into the dissolution [4–7] of gold as well as the electrowinning [8–12] of gold from acidic solutions of thiourea. The use of thiourea introduces a completely novel approach to the hydrometallurgy of gold, since a cationic complex of gold(I) is formed in solution, rather than the anionic complexes obtained by all the other systems for the dissolution of gold.

The redox reaction describing the dissolution of gold in, or its deposition from, acidic thiourea solutions is [13]

$$Au(CS(NH_2)_2)_2^+ + e^- = Au + 2CS(NH_2)_2 \quad (1)$$

and the reduction potential (E_0) was measured to be 0·380 ± 0·010 V at 25°C. The cathodic deposition of gold from acidic solutions of thiourea [8, 10] was reported to occur with a current efficiency of nearly 100% in the over-potential (η) range 0 to −0·4 V, after which hydrogen co-deposition resulted in a decrease in the current efficiency.

The anodic oxidation of thiourea requires one electron per thiourea molecule to yield formamidine disulphide [2, 14, 15]. This couple was considered reversible on platinum [2, 15, 16], with a reduction potential $E_0 = 0{\cdot}420$ V, a value independent of pH over the range 0 to 4·3 [2]; the electrochemical anodic transfer coefficient $\beta \approx 0{\cdot}8$ [14, 15] and the exchange current density $i_0 = (2{\cdot}1 \text{ to } 14{\cdot}7) \times 10^{-6}$ A cm^{-2} [15]. The overall reaction was given as

$$2CS(NH_2)_2 \rightarrow NH_2C(:NH)S.SC(:NH)NH_2 + 2H^+ + 2e^-. \quad (2)$$

Anodic polarization curves have been determined for reactions in 0·25 M sulphuric acid and 0·9 M thiourea [8]; the reactions on platinum and graphite were rapid, but on lead passivation of the electrode occurred. Thiourea was found not to play a significant role in cathodic reactions on platinum, gold or titanium [8].

A review of the redox behaviour of thiourea has been compiled by Gupta [17]; thiourea may be oxidized in successive stages to form a number of products. The first is formamidine disulphide which is formed with relative ease in acidic solutions by the action of oxidants such as hydrogen peroxide [2], and this is followed by slower reactions to form products in which sulphur has a higher oxidation state e.g. sulphur or even sulphate ions. Besides the observation by Preisler [3] that gold electrodes dissolve in acidic solutions of thiourea, no further data could be found regarding the anodic behaviour of gold in this medium. An electrochemical study has therefore been undertaken to investigate the behaviour of gold under controlled hydrodynamic conditions and these results correlated with other electrochemical studies on the deposition of gold from thiourea medium.

2. Experimental

A rotating gold (99·985% pure) disc electrode 1·0 cm in diameter was manufactured from a gold rod mounted closely along the axis of a bell-shaped Teflon holder; this holder could be rotated at fixed speeds of up to 1500 r.p.m. Before immersion in the test solution the surface of the electrode was prepared by mechanical abrasion and immersions successively in acetone, sulphuric acid, hydrochloric acid and doubly distilled water. The potential of the gold electrode was controlled by means of a potentiostat and the current level was usually allowed to reach a constant value for about 10 min before the value was recorded. A saturated calomel electrode (SCE) was used as reference and was connected via a 'Luggin' capillary at the periphery of the Teflon holder.

The difference in potential (E) between the gold electrodes and the calomel electrode ($E_{\mathrm{SCE}} = 0{\cdot}245$ V) was measured by means of a high-impedence electrometer. In this paper all potentials are quoted versus the normal hydrogen electrode (NHE). The auxiliary electrode was a bright platinum foil (about 200 cm^2) which was isolated from the main cell compartment by a sintered glass frit and a gel plug. A large electrochemical cell containing about 1 litre of test solution was used to avoid significant change in the concentrations in the solutions during the experiments, except during the determination of the current efficiency of the dissolution process, when a smaller cell was used containing about 75 ml of test solution.

Experiments were performed at 30°C. All solutions were flushed, usually for at least 2 h, by means of a stream of purified nitrogen before polarization experiments commenced; during the experiments an atmosphere of nitrogen was maintained over the test solutions. Before addition of the electro-active reagents, the test solutions were often scrubbed electrochemically at $\eta \approx -0{\cdot}4$ V. Gold could be added to the solutions in the form of $Au(CS(NH_2)_2)_2.ClO_4$, prepared as a white crystalline salt by the method of Kazakov [13]. Sometimes the gold-thiourea complex was generated electrochemically at an overvoltage of about 0·25 V. Formamidine disulphide was produced *in situ* by the addition of hydrogen peroxide to the acidic solutions of thiourea [2]. Reagent grade chemicals were used, and solutions were made up using doubly distilled water.

The concentration of gold in solution was determined by solvent extraction and atomic absorption spectrometry [18], the pH by means of a glass electrode, and the concentration of thiourea by titration with mercuric nitrate, using diphenylcarbazide as indicator [19].

3. Results

3.1. *Anodic reactions*

Anodic current-potential curves for various concentrations of thiourea in the range 10^{-4} to 10^{-1} M in 0·1 M sulphuric acid are shown in Fig. 1. These curves were unaffected by a change in sulphuric acid concentration in the range 0·01 to 0·1 M, and were also unaffected by a change to perchloric or hydrochloric acid. The current efficiency for the

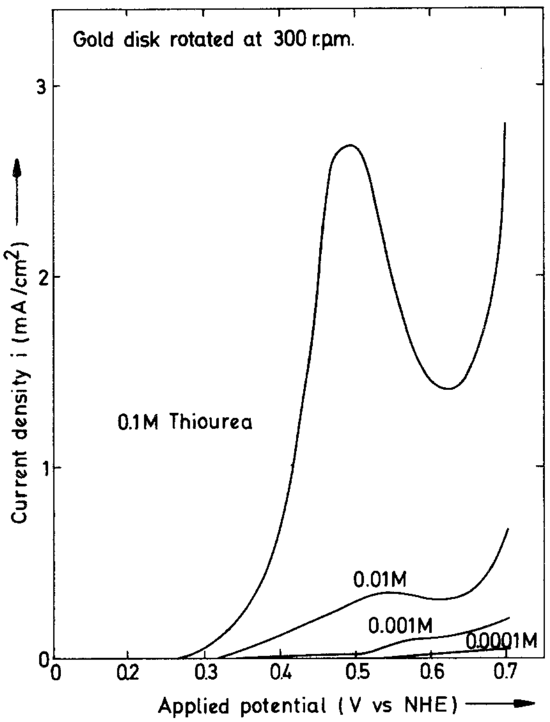

Fig. 1. Effect of the concentration of thiourea upon the anodic dissolution of gold in 0·1 M sulphuric acid at 30°C

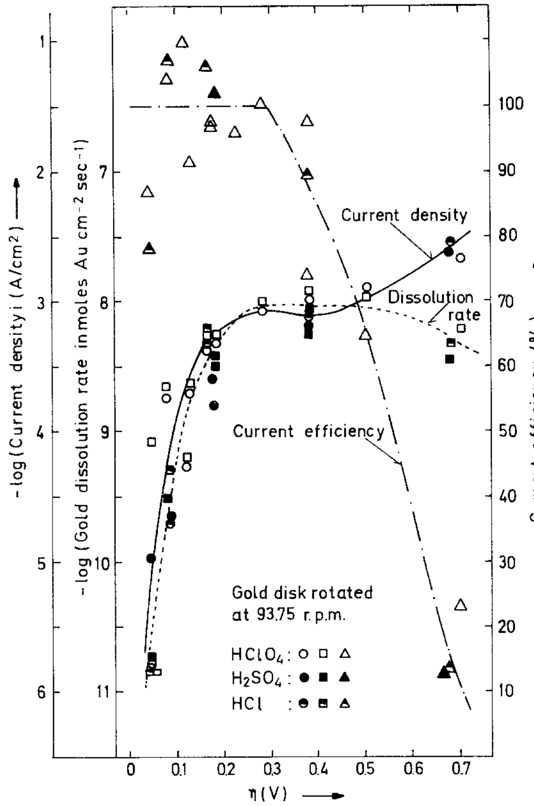

Fig. 2. The anodic dissolution of gold in 0·01 M thiourea and 0·1 M acid at 30°C.

anodic dissolution of gold in 0·1 M thiourea and 0·1 M acid was measured for overpotentials up to $\eta = 0{\cdot}7$ V (Fig. 2). The dissolution proceeded at 100% efficiency up to $\eta \approx 0{\cdot}3$ V and the surface of the gold maintained the normal appearance of etched gold. For values of η greater than about 0·4 V the current efficiency decreased, and the surface of the etched gold appeared to be darkened in patches. While the current density (i) increased for $\eta > 0{\cdot}4$ V, the rate of gold dissolution decreased; under these conditions the potential of a platinum electrode dipped into the anolyte increased with the passage of current through the gold electrode. In accordance with previous work [13] the gold-thiourea perchlorate salt was found to be more stable than the similar compounds of chloride or nitrate. As a result, the more detailed examination of the $i - \eta$ behaviour of gold in thiourea solutions was restricted to perchloric acid media only. A typical set of log i(A cm^{-2}) versus η(V) curves is shown in Fig. 3 (individual readings have been omitted); the gold disk was rotated at 1500 r.p.m. in a solution containing 0·01 M thiourea, 0·1 M perchloric acid and 0·001 M

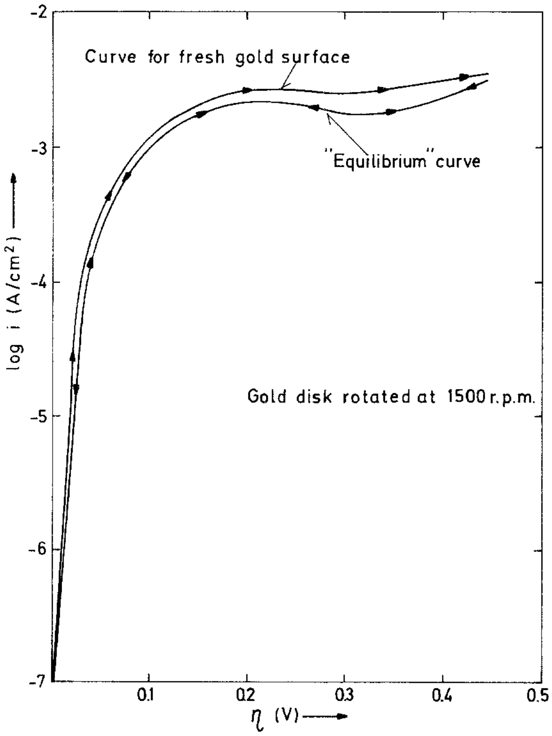

Fig. 3. The anodic dissolution of gold in 0·1 M thiourea, 0·1 M perchloric acid and 0·001 M gold(I)thiourea at 30°C.

Table 1. Anodic dissolution of a rotating gold disc (1500 r.p.m.) at 30°C in thiourea solutions made up to 0·1 M perchloric acid and 0·001 M gold(I)thiourea

Thiourea concentration (C) Molar		*Limiting current (i)* (A/cm² × 10³)		*Butler–Volmer parameters [20]*		
		Measured	*calculated*†	*High field approximation* $i \approx i_0 e^{\alpha F\eta/RT}$		*Low field approximation* $i \approx i_0 F\eta/RT$
				α	i_0 (A/cm² × 10⁶)	i_0 (A/cm² × 10⁶)
0·001	a	0·25	0·507	0·38	44·6	13·8
	b	0·20		0·45	36·2	10·0
0·005	a	1·25	2·54	0·52	97·5	8·0
	b	1·07		0·53	79·4	7·0
0·01	a	2·40	5·07	0·62	98·7	6·12
		0·36*		0·04*	11·8*	1·49*
	b	2·05	5·07	0·70	60·0	3·23
		0·10*		0·04*	11·4*	0·24*
0·03	a	4·0	15·21	0·67	10·9	9·0

* = standard deviation
a = 'initial' curve
b = 'equilibrium' curve
† = Levich relationship [21] $i_{\text{lim}} = 0{\cdot}620\, zFACD^{2/3}\nu^{-1/6}\omega^{1/2}$ mA

gold (I) thiourea at 30° C. The shape of the curve depended upon the history of the experiment. Initially, the trough in the curve at $\eta = 0{\cdot}32$ V was not very pronounced, but as η was changed successively from zero to 0·5 V and back again, the trough deepened and the peak at $\eta = 0{\cdot}22$ V decreased slightly in height. This experiment was repeated four times, and the parameters in the Butler–Volmer equation [20] determined using both the low- and high-field approximations (Table 1). The near-linear plots of i versus the square root of the rate of rotation of the electrode ($\sqrt{\omega}$) shown in Fig. 4 indicated [21] that the reaction was controlled largely by diffusion at the peak of the $i - \eta$ curve.

Further experiments were conducted with solutions in which the thiourea concentrations were 0·001, 0·005 and 0·03 M. With the last solution contamination of the gold surface was rapid, and only the initial curve was completed at overpotentials up to $\eta = 0{\cdot}3$ V; the current at the peak in the curve did not appear to settle down to a constant value. Similar observations were made when the perchlorate salt of the gold(I)thiourea was not recrystallized twice before making up the solution, or if the gold in the solution was generated by anodic dissolution of a gold foil at $\eta = 0{\cdot}25$ V. If η was not increased beyond about 0·2 V during the determination of the $i - \eta$ curves, the poisoning of the gold surface appeared to be a more gradual process.

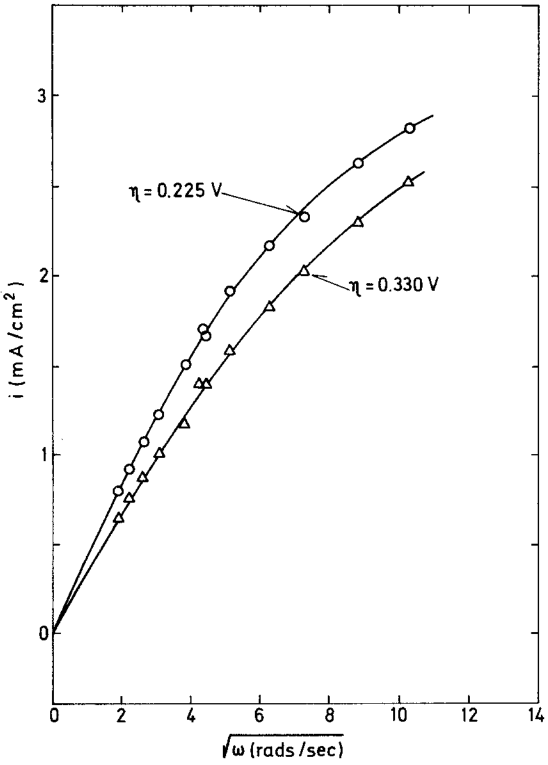

Fig. 4. Dissolution of gold in 0·01 M thiourea, 0·1 M perchloric acid, and 0·001 M gold(I)thiourea at 30°C: Relationship between current density (i) and the rate of rotation of electrode (ω).

The Levich relationship for the rotating disc electrode [21] was used to calculate the limiting current density (i_{lim}), values of which were compared with those measured at the gold disc. The kinematic viscosity (ν) of these solutions was measured (9×10^{-3} cm^2 s^{-1}) and it was assumed that the diffusion coefficient (D) of thiourea was $1{\cdot}53 \times 10^{-5}$ cm^2 s^{-1} at 30°C (medium unspecified) [22] and that two molecules of thiourea were required for each molecule of gold dissolved, that is $z = 2$.

The results are summarized in Table 1.

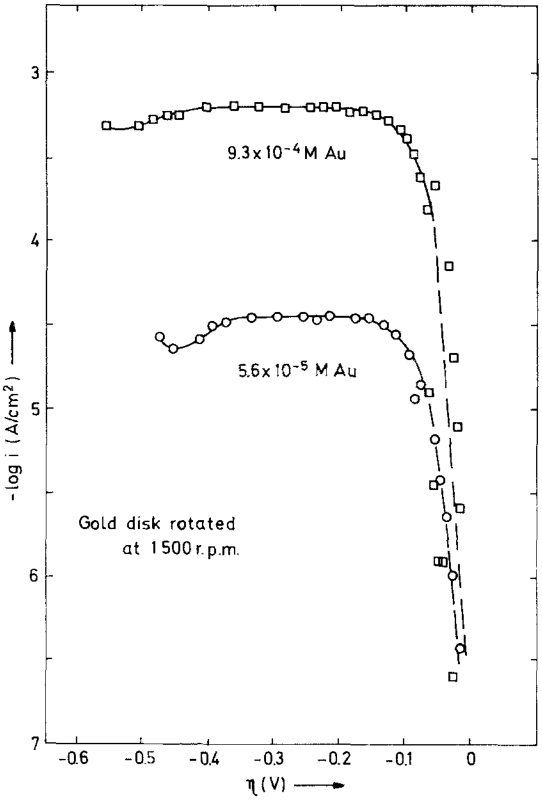

Fig. 5. Cathodic deposition of gold from solution containing 0·01 M thiourea and 0·1 M sulphuric acid at 30°C.

3.2. *Cathodic reactions*

Polarization curves for the deposition of gold from 0·01 M thiourea and 0·1 M perchloric acid are shown in Fig. 5. Similar results were obtained both in a sulphuric acid medium and when the concentration of thiourea was varied between the limits 0·001 to 0·05 M. The results obtained in the range $\eta = 0{\cdot}0$ to $-0{\cdot}1$ V tended to be somewhat irreproducible, particularly when the solution was made up with electrochemically-generated gold or with an impure gold(I)thiourea perchlorate salt. In these circumstances it was possible only to estimate the values of the transfer coefficient $\alpha = 0{\cdot}4$ (standard deviation, $\sigma = 0{\cdot}07$) and the exchange current density $i_0 = 1{\cdot}2 \times 10^{-4}$ A cm^{-2} ($\sigma = 0{\cdot}2 \times 10^{-4}$ A cm^{-2}). Reproducible results were obtained over the range $\eta = -0{\cdot}15$ to $-0{\cdot}6$ V, the plateau at $\eta = -0{\cdot}15$ to $-0{\cdot}3$ V being followed by a trough at $\eta = -0{\cdot}35$ to $-0{\cdot}55$ V. The rate of deposition was found to be diffusion-controlled at $\eta = -0{\cdot}2$ V, but controlled only partially by diffusion at $\eta = -0{\cdot}425$ V (Fig. 6). The diffusion coefficient, D, of $\text{Au(CS(NH}_2)_2)_2^+$ at 30°C was calculated using the Levich [21] relationship and assuming $\nu = 9 \times 10^{-3}$ cm^2 s^{-1}. It was found that $D = 1{\cdot}1 \times 10^{-5}$ cm^2 s^{-1} in 0·01 M thiourea and 0·1 M sulphuric or perchloric acid. This value of D compared favourably with the value reported previously [9] of $1{\cdot}17 \times 10^{-5}$ cm^2 s^{-1} at 50°C in 0·25 M sulphuric acid and 1 M thiourea.

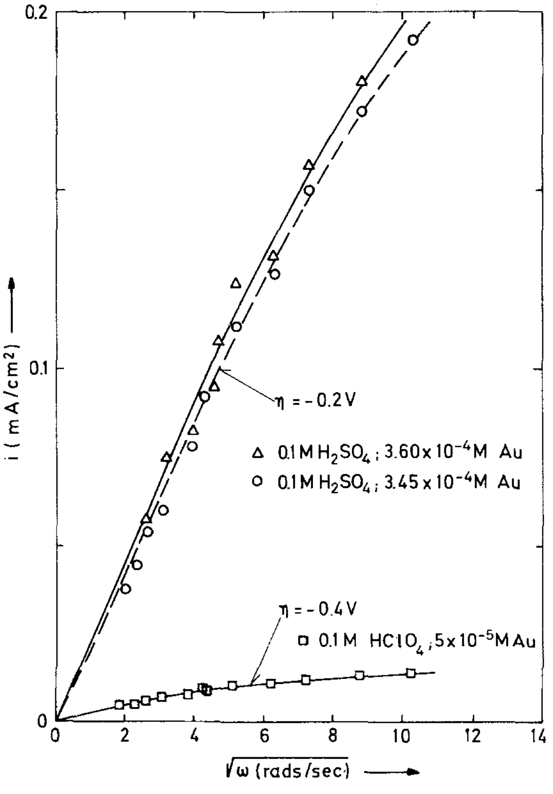

Fig. 6. Deposition of gold from 0·01 M thiourea and 0·1 M acid at 30°C: Relationship between current density (i) and the rate of rotation of the electrode (ω).

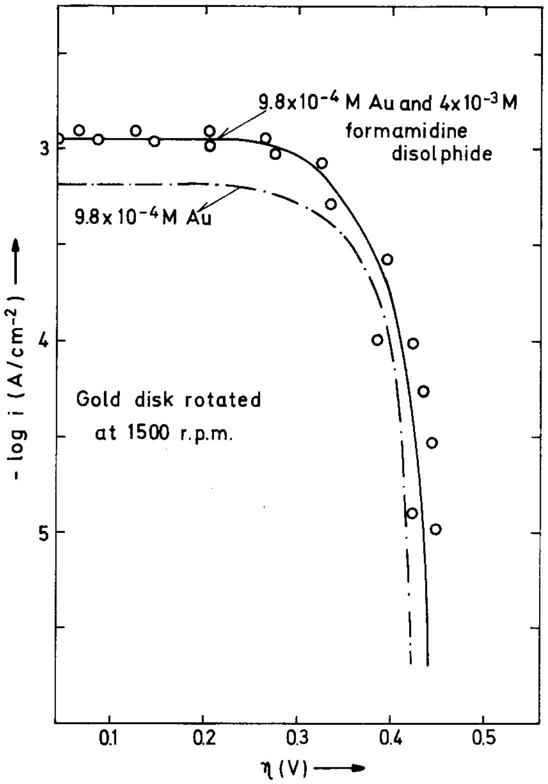

Fig. 7. Cathodic behaviour of formamidine disulphide in 0·01 M thiourea and 0·1 M perchloric acid containing gold(I)thiourea at 30°C.

The shape of the cathodic $i - \eta$ curves tended to be altered by the presence in the solution of hydrogen peroxide or formamidine disulphide (Fig. 7). In a solution containing both gold and formamidine disulphide, the current readings were very irreproducible in the range η = 0·0 to −0·1 V but over the remainder of the range of η reproducible results were obtained. Although the reduction of both gold(I)thiourea and formamidine disulphide appears to occur simultaneously on the surface of gold, diffusion control cannot be assumed for both reactions. On the assumption that two electrons were produced for each formamidine disulphide molecule reduced to thiourea, calculation of the diffusion coefficient of formamidine disulphide gives a value of 3×10^{-7} cm^2 s^{-1}, which is clearly too low. The gold electrode appeared to be darker in colour at the end of this experiment than was usual for gold deposited from thiourea solutions.

In acidic solutions containing only thiourea and formamidine disulphide the cathodic current values tended to decrease steadily and the reduction of formamidine disulphide on gold was soon inhibited completely. In the presence of gold(I)thiourea in the solution, the surface of the gold is renewed constantly, and formamidine disulphide can be reduced continually at this surface.

3.3. *Reduction potentials*

The standard reduction potential of Equation 1 was calculated from the appropriate form of the Nernst equation, $E_0 = E - E_{\mathrm{SCE}} - 0{\cdot}0606 \log [\mathrm{Au(I)}]/[\mathrm{CS(NH_2)_2}]^2$

When a freshly prepared gold disc was immersed in a solution containing carefully prepared reagents, E_0 = 0·352 V (standard deviation σ 0·007 for 17 determinations) for gold concentrations of about 10^{-3} M and thiourea concentrations ranging from 10^{-3} to 3×10^{-2} M. If the gold electrode had been kept at $\eta < 0{\cdot}4$ V for an appreciable time, as, for example, during the determination of the current efficiency of the dissolution process, and then used to determine the equilibrium potential, E_0 = 0·372 V (σ = 0·006 V for 10 determinations), and if $0{\cdot}4\text{ V} < \eta < 0{\cdot}7$ V, E_0 = 0·41 V(σ = 0·02 V for three determinations). During these experiments the gold(I)thiourea content varied between 2×10^{-6} and 3×10^{-4} M, and was generated electrochemically in the 0·01 M thiourea and 0·1 M acid. Similar results were obtained in sulphuric, hydrochloric or perchloric acid media.

4. Discussion

4.1. *Anodic reactions*

The rate of anodic dissolution appears to be reduced by the presence in the solution of substances which may be introduced as impurities in the reagents used to make up the solutions, or which are generated during the anodic processes on the surface of the gold. At values of η of up to 0·25 V, the rate of dissolution of each atom of gold is dependent largely upon the rate of diffusion of two molecules of thiourea at the surface of the gold ($i_{\mathrm{lim\ measured}} \approx$ $\approx i_{\mathrm{lim\ calculated}}$). At higher values of η, the excess current contributes to reactions involving the oxidation of thiourea such as, for example, the formation of formamidine disulphide which will consume one electron per molecule of thiourea, confirmed by the increase in the solution potential, or the production of sulphur which will require two electrons, and so on. The appearance of dark films on the etched gold surface at these higher potentials indicates also the probable formation of gold sulphides. At the lower potentials at which gold dissolves at a maximum rate ($\eta = 0{\cdot}22$ V) the surface of the gold is being renewed constantly, and the effect of such surface films may be reduced. This may account for the value of i_0 measured at $\eta = 0{\cdot}075$ V being larger than the value determined at $\eta \leqslant 0{\cdot}01$ V, where the rate of renewal of the gold surface may be too low to overcome the adsorption of contaminants.

While there may be uncertainty regarding the actual value of i_0, it is fairly certain that $i_0 > 10^{-6}$ A cm^{-2}, which indicates that the dissolution of gold in acidic thiourea solutions is a reversible electrochemical process.

4.2. *Cathodic reactions*

Bek [8] described the polarization curves for the deposition of gold from acidic solutions of thiourea. At the peak in the curves at $\eta = -0{\cdot}20$ V, the rate of gold deposition was controlled by diffusion (activation energy E_a = 6 to 7 Kcal mole^{-1}), and at the trough in the curve at $\eta = 0{\cdot}35$ to 0·40 V, the reaction was controlled by an electrochemical reaction (E_a = 17 to 20 Kcal mole^{-1}). The peak current increased when the concentration of thiourea in the solution increased from 0·13 to 1·16 M, and this was ascribed to a catalytic effect upon the rate of gold deposition by impurities in the thiourea [8]. However, it is impossible to catalyse a diffusion-controlled reaction in this manner, and it is more likely that the increase in the current was due to the electro-reduction of these impurities, e.g. formamidine disulphide, the existence and nature of which was not known by this school of workers [9] This assumption is supported by the fact that even at the peak in the curve, the current efficiency of the deposition of gold did not reach 100% [8, 10]. In these studies the solutions of gold(I)thiourea were usually prepared using gold(III)salts, which are reduced by thiourea to gold(I) [23, 24]; thus additional oxidation products of thiourea from this source too had to be present in these [8, 10] solutions.

4.3. *Reduction potentials*

The value of the standard electrode potential (E_0) measured on a gold electrode depends upon the extent of contamination of the surface. This could explain the wide range of values (E_0 from 0·336 to 0·395 V) obtained by Kazakov [13] in 10^{-3} M Au(I) solution as the concentration of thiourea increased from 10^{-4} to 2×10^{-1} M; a change in E_0 such as this could also be due to the presence of more than one complex thiourea ion of gold, but no evidence of the existence of ions other than $Au(CS(NH_2)_2)_2^+$ has been reported.

5. Conclusions

Acidic solutions of thiourea can be considered as a non-toxic alternative to cyanide for electropolishing of gold surfaces. Further investigations are necessary to reveal the extent of control of the current density distribution over the gold surface required to avoid etching of the surface on the one hand, and darkening of the surface due to thiourea decomposition on the other.

While the effectiveness of acidic solutions of thiourea has been demonstrated in hydrometallurgical applications such as the dissolution of gold from crushed ore bodies [5], excessive consumption of thiourea during the process will depend upon whether an oxidant can be found which can oxidize the gold metal to the gold(I)state, but which does not cause excessive oxidation or degradation of the thiourea. The relative proximity of the standard reduction potentials for the redox couples gold(I)-thiourea/gold (E_0 = 0·352 V on gold) and formamidine disulphide/thiourea (E_0 = 0·430 V on platinum [2]) can be used as guide to the selection of such an oxidant; the formation of formamidine disulphide itself need not be avoided, since its presence still promotes the dissolution of gold in solutions of thiourea [2]. However, the next stage in the decomposition of thiourea would be the formation of elemental sulphur, which could not contribute to the dissolution mechanism for gold. Further studies on the use of chemical oxidants in acidic solutions of thiourea have been made [25], and these have confirmed that the slight poisoning of the gold surface does not permit the maximum diffusion limiting rate to be achieved.

The cathodic deposition of gold from acidic solutions of thiourea can be used for the recovery of gold from such solutions or for the production of gold plate. A number of advantages may arise. The overpotential for the cathodic evolution of hydrogen is increased markedly in the presence of thiourea (at least on silver [26]) so that the problem of polymer formation [27] in the gold electroplate is not as likely to arise as when acidic cyanide solutions are used. Also, thiourea solutions containing dissolved oxygen are not solvents for gold metal and the need for degassing the solution can be avoided [25].

The disadvantages of a thiourea plating process for gold may lie in the possibility that sulphur may be incorporated in the gold electroplate. If, however, the presence of the oxidation products of thiourea can be avoided by the use of pure reagents and by effective separation of the anode and cathode compartments, this problem may not arise at all.

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