*Inorg. Chem.* **2004**, *43*, 3048–3056

Inorganic Chemistry
Article

# The Ammine, Thiosulfato, and Mixed Ammine/Thiosulfato Complexes of Silver(I) and Gold(I)

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Received November 10, 2003

The M(I)–$NH_3$, M(I)–$S_2O_3^{2-}$, and M(I)–$S_2O_3^{2-}$–$NH_3$ systems (M = Ag, Au) were studied at 25 °C and at $I = 0.1$ M ($NaClO_4$) using a variety of analytical techniques. For the Ag(I)–$NH_3$–$S_2O_3^{2-}$ system, $AgS_2O_3NH_3^-$ was detected with formation constant log $\beta_{111}$ (for the reaction $Ag^+ + S_2O_3^{2-} + NH_3 \leftrightarrow AgS_2O_3NH_3^-$) of 11.2, 10.4, and 10.8 on the basis of silver potentiometry, UV–vis spectrophotometry, and hydrodynamic voltammetry, respectively. Also, the values of log $\beta_{101}$($AgNH_3^+$), log $\beta_{102}$($Ag(NH_3)_2^+$), log $\beta_{110}$($AgS_2O_3^-$), and log $\beta_{120}$($Ag(S_2O_3)_2^{3-}$), obtained from silver potentiometry, were 3.59, 7.0, 8.97, 13.1, respectively. In the case of the ammine complexes, the log $\beta_{101}$($AgNH_3^+$) and log $\beta_{102}$($Ag(NH_3)_2^+$) values were found to be 3.5 and 7.1, respectively, from the UV–vis spectrophotometric experiments. The mixed species $AuS_2O_3NH_3^-$ was detected in UV–vis spectrophotometric, hydrodynamic voltammetric, and potentiometric experiments with the stepwise formation constants (log $K_{111}$) of –4.0, –3.5, –3.8, respectively, for the reaction $Au(S_2O_3)_2^{3-} + NH_3 \leftrightarrow AuS_2O_3NH_3^- + S_2O_3^{2-}$. At higher [$NH_3$]/[$S_2O_3^{2-}$] ratios (>$10^5$), the formation of $Au(NH_3)_2^+$ was also detected in spectrophotometric and potentiometric experiments with stepwise formation constants (log $K_{102}$) of –5.4 and –5.3, respectively, according to the reaction $AuS_2O_3NH_3^- + NH_3 \leftrightarrow Au(NH_3)_2^+ + S_2O_3^{2-}$.

## Introduction

Silver(I)– and gold(I)–thiosulfato complexes have applications in photography,[1,2] gold and silver extractive metallurgy,[3] industrial plating processes,[4] and medicine.[5–7] A knowledge of the nature of the chemical species of Ag(I) and Au(I) in ammoniacal thiosulfate solutions is useful for the understanding of the chemistry of these metal thiosulfate–ammine interactions and the leaching and recovery of these metals using hydrometallurgical processes. In the ammoniacal silver(I) system, two mixed complexes, $AgS_2O_3NH_3^-$ and $AgS_2O_3(NH_3)_2^-$, have been reported in a mixed ligand system which contained $NH_3$, $S_2O_3^{2-}$, and $SCN^-$.[8] As for gold(I), only some studies adverting to this system could be found.[9] The high stability of the di-thiosulfato complex[10] and the instability of free $Au^+$ ions with respect to disproportionation[11] (3Au(I) → 2Au(0) + Au(III)) make it difficult to conduct suitable experiments. Nevertheless, on the basis of the $Au^+/Au^0$ standard reduction potential estimate of 1.7 V,[12] the formation constant values of $Au(NH_3)_2^+$ (log $\beta_{102} = 19.5$, 25 °C, $I = 10$ M ($NH_4NO_3$))[11] and $Au(S_2O_3)_2^{3-}$ (log $\beta_{120} = 26.0$, 25 °C, $I = 1$ M (KCl))[10] have been reported.

In characterizing the various species that would form in ammoniacal Ag(I)–$S_2O_3^{2-}$ solutions, the Ag(I)/$NH_3$ and Ag/$S_2O_3^{2-}$ systems were re-evaluated at $I = 0.1$ M $NaClO_4$ using Ag potentiometry, UV–vis spectrophotometry, and hydrodynamic voltammetry. The same techniques were used with

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10.1021/ic035301z CCC: $27.50 © 2004 American Chemical Society
Published on Web 04/23/2004

the mixed ligand ($NH_3-S_2O_3^{2-}$) systems of Ag(I) and Au(I). Due to the instability of $Au^+$, $Au(S_2O_3)_2^{3-}$ was used as the starting material with the determination of the stepwise formation constants between the various species of Au(I).

## Experimental Section

**Materials.** Reagents were made with calibrated grade A volumetric glassware using high purity water (Millipore, Milli-Q system) deaerated with high purity $N_2$ to minimize $CO_2$ contamination. High spectral purity $NaClO_4$ (Aldrich Chemical Co., "99.99%" grade) was used as the swamping electrolyte source to maintain a constant ionic strength. Both the $NaClO_4$ and $HClO_4$ stock solutions were prepared and standardized as described elsewhere.[13] Ammonia stock solutions (∼2.0 M) were prepared from concentrated ammonia solution (25% BDH, AR, U.K.) and standardized (±0.1%) against 1.0 M HCl (BDH, U.K., concentrated volumetric standard) with methyl orange as the indicator.[14] The $AgClO_4$ stock solutions (∼0.01 M) were prepared by dissolving solid $AgClO_4$ (BDH, AR, U.K.). The concentration of $Ag^+$ was determined (±0.2%) titrimetrically against EDTA (BDH, U.K., concentrated volumetric standard) after the addition of excess potassium tetracyanonickelate(II) in the presence of an ammonia−ammonium chloride buffer with Murexide as the end point indicator.[14] Stock solutions of $Na_3Au(S_2O_3)_2$ and $Na_2S_2O_3$ (∼0.1 M) were prepared by dissolving accurately weighed $Na_3Au(S_2O_3)_2$(s) (Alfa-Aesar, AR, U.S.A.) and $Na_2S_2O_3$(s) (BDH, AR, U.K.) using a Sartorius weighing balance (2024MP max 100 g ± 0.01 mg). The purity of $Na_2S_2O_3$ stock solutions was determined using the standard iodometric (±0.2%) titration.[14] Analytical grade $NH_4ClO_4$ was prepared by slowly neutralizing a 2 M $HClO_4$ solution with excess $NH_3$(aq) solution and then boiling and drying the product in a vacuum oven at 80 °C. Caution was taken here as $NH_4ClO_4$ is explosive when heated.

**UV−Vis Spectrophotometric−Potentiometric Experiments.** Simultaneous UV−vis spectrophotometric−potentiometric experiments were conducted for the Ag(I)−$NH_3$, Ag(I)−$S_2O_3^{2-}$−$NH_3$, and Au(I)−$S_2O_3^{2-}$−$NH_3$ systems using the apparatus setup described previously.[13] Absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer using the specially constructed cell with an optical path length of 0.74 ± 0.01 cm used for the Ag(I) experiments and 10.76 cm used for the Au(I) experiments. The hydrogen ion and $Ag^+$ or $Au^+$ potentials were measured in situ using a calibrated glass electrode (Metrohm, model 6.0101.000) and a clean calibrated Ag or Au wire electrode, respectively. The potentials were measured against the Ag(0)/AgCl(s)/$Cl^-$(aq)/0.1 M $NaClO_4$ salt bridge/reference electrode using a dual input high impedance digital voltmeter (±0.1 mV) of in-house construction. All titrations were performed under $N_2$ with temperature maintained at 25.0 ± 0.05 °C, and titrant was manually added from a piston buret (Metrohm Dosimat, model 665, calibrated accuracy ±0.1%). Electrode potentials and the absorption spectra were recorded after 1−5 min of equilibration with each addition of titrant.[13]

The Ag(I)−$NH_3$ complexation titrations were conducted by titrating into starting solutions of 0.5 mM $AgClO_4$, 0.01 M $HClO_4$, 0.08 M $NaClO_4$, and 0.01 M $NH_4ClO_4$ titrant similar to the starting solution containing 0.01 M NaOH instead of 0.01 M $HClO_4$. Titrations of similar solutions without Ag(I) were used to obtain spectra for the background corrections, and the first potentials of the Ag(I) starting solution were used to calibrate both the glass and the silver electrodes. For the Ag(I)−$S_2O_3^{2-}$−$NH_3$ experiments, starting solutions of 0.5 mM $AgClO_4$, 0.1 M $NaClO_4$, and $Na_2S_2O_3$ (0.01, 0.015, and 0.02M) were titrated with similar solutions containing 0.1 M $NH_3$. Spectra were recorded against water with the spectrum of $Na_2S_2O_3$(aq) (0.1 M) recorded separately and factored in the calculations.

As for the Au(I)−$S_2O_3^{2-}$−$NH_3$ experiments typically, starting solutions were made in situ by adding small accurately weighed quantities of $Na_3Au(S_2O_3)_2$. The spectrum and gold potential values were recorded after each addition of $Na_2S_2O_3$(s) followed by fixed volumes of concentrated $NH_3$(aq) (∼11 M) in 0.1 M $NaClO_4$. Additional Au(I) potentiometric data were obtained from rest potential values during the hydrodynamic voltammetry experiments (see below) using a rotating gold disk electrode.

Separate silver potentiometric titrations were conducted for the silver−thiosulfate system using an autotitrator setup[15] with potentials recorded after 1 min of equilibration. For this experiment, 0.01 M $AgClO_4$ and 0.1 M $NaClO_4$ were titrated into 50 mL aliquots of starting solutions containing 0.01 M $Na_2S_2O_3$ and 0.1 M $NaClO_4$.

Data analysis for the spectrophotometric experiments were performed using the computer program SPECFIT,[13,16,17] and the value of p$K_a$ ($NH_4^+$) was taken as 9.1 as derived from the potentiometric study (Table 1). For all the data analysis in this report, the value of p$K_w$ at $I = 0.1$ M ($NaClO_4$) was taken to be 13.75.[18] The potentiometric data for the Ag(I)−$NH_3$, Ag(I)−$S_2O_3^{2-}$−$NH_3$ systems were analyzed using the ESTA[19] suite of software. In the case of the Au(I)−$S_2O_3^{2-}$−$NH_3$ system, the hydrodynamic rest potentials were analyzed graphically, and the potentiometric data from the simultaneous UV−vis experiments were analyzed using SPECFIT.[13,16,17] For the latter data, the antilogs of the potential values were used to simulate the spectral response of $Au^+$, and the stepwise formation constants (log $K_{hij}$) between the two complexes present were calculated. The best model used for the data analysis was decided on the basis of the best fit from a variety of chemically sensible models described by a minimum objective function. Unless otherwise stated, the stability constant log $\beta_{hij}$ of each complex $M_hX_iY_j^{+(nh-bi-cj)}$ was calculated using eq 2.

$$hM^{+n} + iX^{-b} + jY^{-c} \Leftrightarrow M_hX_iY_j^{+(nh-bi-cj)} \quad (1)$$

$$\log \beta_{hij} = \log\{[M_hX_iY_j^{+(nh-bi-cj)}]/[M^{+n}]^h[X^{-b}]^i[Y^{-c}]^j\} \quad (2)$$

**Hydrodynamic Voltammetry.** The hydrodynamic voltammetry (HV) experiments were performed using a voltammetry stand of in-house construction consisting of a rotating electrode setup dipping into a double walled 50 mL electrochemical cell. The cell temperature was maintained at 25 ± 1 °C with a circulation water system (Ratek isothemal bath). The electrode rotation speed for the experiments was maintained at 1000 ± 5 rpm. The current measurements in the ∼50 μA range were carried out using a RDE3 scanner (Pine Instruments) with a potential sweep of 5 mV/s, and results were automatically recorded at about 5 data points/s in a personal computer using a LABView written program. Measure-

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**Table 1.** log $\beta_{pq}$ Values of the Ag(I)− and Au(I)−Thiosulfate−Ammonia System at 25 °C

| $I$ ($NaClO_4$)/M | $pK_a$ ($NH_4^+$) | log $\beta^a$ $Ag(NH_3)^+$ | log $\beta^a$ $Ag(NH_3)_2^+$ | log $\beta^a$ $Ag(S_2O_3)^-$ | log $\beta^a$ $Ag(S_2O_3)_2^{3-}$ | log $\beta^a$ $Ag(S_2O_3)$-$(NH_3)^-$ | log $K_{111}{}^c$ $Au(S_2O_3)$-$(NH_3)^-$ | log $K_{102}{}^d$ $Au(NH_3)_2^+$ | method$^e$ | ref$^f$ |
|---|---|---|---|---|---|---|---|---|---|---|
| ∼0 | 9.2 | 3.3 | 7.2 | | | | | | P | 22 |
| 0.1 | 9.25 | 3.23 | | | | | | | P | 23 |
| 0.5 | | 3.36 | 7.38 | | | | | | P | 24 |
| ∼0 | | | | 8.8 | | | | | P | 25 |
| ∼0 | | | | | 13.6 | | | | P | 22 |
| 0.1 | 9.10 ± 0.03$^b$ | 3.59 ± 0.01$^b$ | 7.04 ± 0.09$^b$ | | | | | | P | |
| 0.1 | | 3.5 ± 0.1 | 7.13 ± 0.07 | | | | | | S | |
| 0.1 | | | | 8.97 ± 0.01 | 13.09 ± 0.02 | | | | P | |
| 0.1 | | | | | 13.0 ± 0.4 | 10.8 ± 0.4 | | | V | |
| 0.1 | | | | | | 11.2 ± 0.1 | | | P | |
| 0.1 | | | | | | 10.4 ± 0.3 | | | S | |
| 0.1 | | | | | | | −4.0 ± 0.2 | −5.4 ± 0.4 | S | |
| 0.1 | | | | | | | −3.5 ± 0.2 | | V | |
| 0.1 | | | | | | | −3.8 ± 0.2 | −5.3 ± 0.4 | P | |

[a] Formation constants of complexes as defined in eq 2 (log $\beta_{pq}$). [b] Uncertainties expressed as the range of the average log $\beta_{pq}$ values. [c] Formation constants of the $Au(S_2O_3)(NH_3)^-$ complex as defined in eq 14. [d] Formation constants of the $Au(NH_3)_2^+$ complex as defined in eq 15. [e] P = potentiometry; S = spectrophotometry; V = voltammetry. [f] This study unless stated otherwise.

ments for the Au(I) system were made using a rotating gold disk electrode (3 mm diameter) while for the Ag(I) system a silver disk electrode (1.5 mm diameter) and a platinum disk electrode (2 mm diameter) were used. Starting solutions of 25−50 mL of 0.1 M $NaClO_4$ and ∼ 3 mM $AgClO_4$(aq) were pipetted into the cell, and $N_2$ bubbling was introduced prior to the addition of $NH_3$ to the required concentration of 1.7 M. During the experiments, a $N_2$ blanket was maintained over the solution, and the concentration of $S_2O_3^{2-}$ was varied by the stepwise addition of accurately weighed quantities of sodium thiosulfate crystals (∼3 mg). Similar experiments were conducted for the Au(I) system using starting solutions consisting of gold thiosulfate (∼4 mg) in 25−50 mL of 0.1 M $NaClO_4$, 0.01 M NaOH, and $NH_3$(aq) (0.3−7 M).

By combining the general current−potential equations for a rotating disk electrode, the Levich and the Nernst equations, the $E_{1/2}$ reduction potential of the complex $MX_iY_j$ to M and $M^{+n}$ to M on the surface of the rotating disk electrode at a constant rotation speed[20] can be expressed by eqs 5 and 6

$$M^{+n} + ne^- \leftrightarrow M(\text{on electrode}) \tag{3}$$

$$MX_iY_j^{(+n-ib-jc)} + ne^- \leftrightarrow M(\text{on electrode}) + iX^{-b} + jY^{-c} \tag{4}$$

$$(E_{1/2})_S = E° + (RT/0.4343nF)\log(I_M[M^{+n}]/I_S[M]) \tag{5}$$

$$(E_{1/2})_C = E° + (RT/0.4343nF)\log(I_M[MX_iY_j^{(+n-ib-jc)}]/I_C[M]) \tag{6}$$

where [M] is the concentration of metal deposited on the rotating electrode, $I_M$ is the limiting current caused by the metal deposition, and $(E_{1/2})_C$, $I_C$, $(E_{1/2})_S$, $I_S$ are the half wave potentials and limiting currents for the reduction of $MX_iY_j^{(+n-ib-jc)}$ to M and $M^{+n}$ to M, respectively. Hence, at 25°C

$$(E_{1/2})_C - (E_{1/2})_S + (0.0592/n)\log(I_C/I_S) = (0.0592/n)\log\{\beta_{1ij} + i\log[X^{-b}] + j\log[Y^{-c}]\} \tag{7}$$

where

$$\beta_{1ij} = [MX_iY_j^{(+n-ib-jc)}]/[X^{-b}]^i[Y^{-c}]^j \tag{8}$$

The limiting currents ($I_C$) were estimated from current ($i$)−potential ($E$) curves and half wave Au potentials ($E_{1/2}$) from plots of $E$ against $\log\{i/(I_C - i)\}$ since[20]

$$E = E_{1/2} - 0.0592/n \log\{i/(I_C - i)\} \tag{9}$$

Since only relative $E_{1/2}$ values were used in the analysis, it was found that an easier determination of $E_{1/2}$ could be obtained by reading off charts of $E$ versus a moving point average of d$i$/d$E$ with a period of 20 points calculated using the spreadsheet software. Here, $E_{1/2}$ is at minimum; the peak heights are proportional to the limiting current, and the relation between the two (eq 10) provides a method to test the reversibility of the system.[21]

$$\{di/dE\}E_{1/2} = -(nF/4RT)I_C \tag{10}$$

Since $I_S \approx I_C$, for most of the results a further simplification of eq 8 was made as 0.0592 $\log(I_S/I_C)$ approaches zero. A plot of $(E_{1/2})_C$ versus $\log[X^{-b}]$ or $\log[Y^{-c}]$ was used to estimate the coordination number $i$ and $j$, and the formation constants of the species formed were deduced using $E_{1/2}$ at $[X^{-b}]$ or $[Y^{-c}]$ = 1 M. Since the value of $E_{1/2}$ for $Au^+$/Au is unobtainable due to the instability of $Au^+$(aq), the difference between $(E_{1/2})_C$ for the two complexes C1 and C2 was used to estimate the stepwise formation constant ($K_q$) for the following reaction:

$$MX_pY_q^{(+n-pb-qc)} + iX^{-b} + jY^{-c} \leftrightarrow MX_{(p+i)}Y_{(q+j)}^{\{+n-(p+i)b-(q+j)c\}} \tag{11}$$

$$(E_{1/2})_{C1} - (E_{1/2})_{C2} = (0.0592/n)\log\{K_{1ij} + i\log[X^{-b}] + j\log[Y^{-c}]\} \tag{12}$$

where

$$K_{1ij} = [MX_{(p+i)}Y_{(q+j)}^{\{+n-(p+i)b-(q+j)c\}}]/[MX_pY_q^{(+n-pb-qc)}][X^{-b}]^i[Y^{-c}]^j \tag{13}$$

## Results

**Ag(I) −$S_2O_3^{2-}$−$NH_3$ Potentiometry.** Only two silver(I) ammine complexes have been reported,[22−24] and hence,

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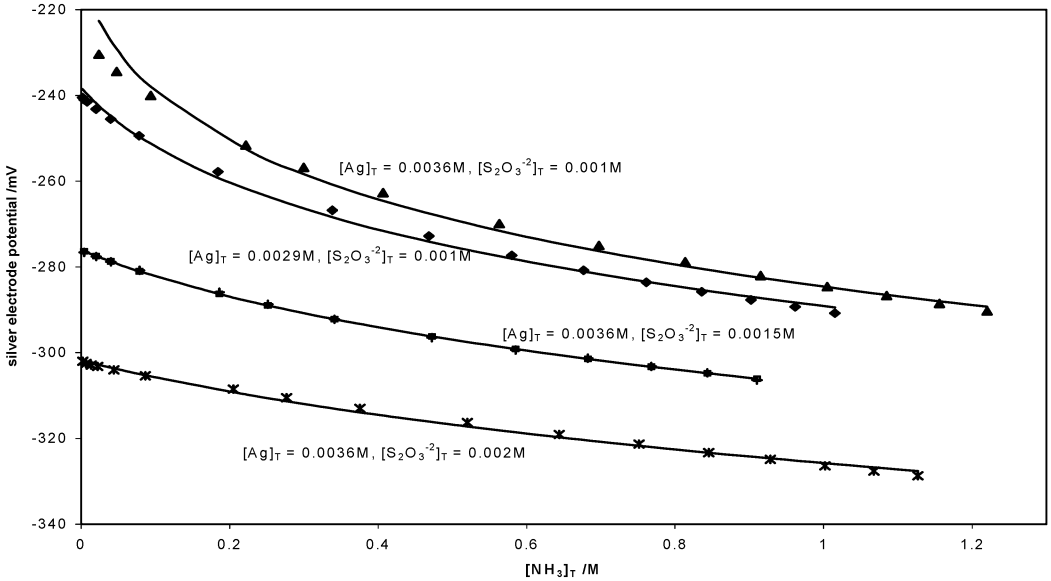

**Figure 1.** Results of the Ag(I)$-NH_3-S_2O_3^{2-}$ potentiometric experiments. Markers are the raw data points while the lines are the fits from ESTA, assuming $Ag(S_2O_3)(NH_3)^-$.

designators for $AgNH_3^+$ and $Ag(NH_3)_2^+$ were used in the model to simulate the electrode potentials simultaneously obtained during the spectrophotometric titrations for the Ag(I)$-NH_3$ experiments (Figure S1). The stability constants obtained in this work were consistent with the literature (Table 1). To get a good fit, the initial p$K_a$ value of $NH_4^+$ (9.25, $I = 0.1$ M $NaClO_4$) was also optimized. The stability constants obtained in this study (Table 1) were subsequently used in the calculations for the experiments on the Ag(I)$-S_2O_3^{2-}-NH_3$ system.

For the Ag(I)$-$thiosulfate potentiometric titrations, only titrations where $AgClO_4$(aq) was added to excess $S_2O_3^{2-}$ could be performed as irreversible precipitation products (presumably $Ag_2S$(s)) formed whenever $[Ag(I)]_T$ was in excess. Although there have been reports of the formation of $Ag(S_2O_3)_3^{5-}$,[22] for the concentration range used in this experiments, the use of only $Ag(S_2O_3)^-$ and $Ag(S_2O_3)_2^{3-}$ designations in the model were sufficient to give results (Figure S2) in reasonable agreement with literature[22,25] (Table 1). These values were found to be critical in the subsequent calculations related to the Ag(I)$-S_2O_3^{2-}-NH_3$ system.

It has been reported that the formation of both $Ag(S_2O_3)(NH_3)^-$ and $Ag(S_2O_3)(NH_3)_2^-$ with log $\beta_{111} = 9.88$ and log $\beta_{112} = 13.0$ at $I = 1.0$ $KNO_3$, 25 °C, occurs in ammoniacal silver thiosulfate solutions in a study of the three ligand system $NH_3$, $S_2O_3^{2-}$, and $SCN^-$.[8] However, a good fit of the potentiometric data in this study could be accomplished by using a model containing just the single complex species $Ag(S_2O_3)(NH_3)^-$ (Figure 1). Forcing the convergence of the model by incorporating $Ag(S_2O_3)(NH_3)_2^-$ gave an order higher objective function (sum of variances = 5$-$150) with no significant difference in the derived stability constant value. This indicates a poor fit of the literature model,[8] with the experimental data in the present study at $I = 0.1$ M.

**Ag(I) $-S_2O_3^{2-}-NH_3$ UV$-$Vis Spectrophotometry.** A typical series of background subtracted spectra at the pH range 2$-$8.9 showed significant spectral changes suggesting the presence of only three species including $Ag^+$. These spectra were time independent, and up to moderate $OH^-$ concentrations (pH $\leq$ 9), the SPECFIT analysis of the absorbances from 216 to 300 nm was consistent with the presence of $Ag^+$, $AgNH_3^+$, and $Ag(NH_3)_2^+$. By fixing the p$K_a$ of $NH_4^+$ to that obtained from the potentiometric data, the calculated stability constants according to this model compared well with the published constants as well as the values from the potentiometric work (Table 1). The acquired deconvoluted charge transfer spectra of the various Ag(I) species are shown in Figure 2.

With the inclusion of $S_2O_3^{2-}$ in the Ag(I)$-NH_3$(aq) experiments, a mixed species was inferred by observing the changes in the UV spectra of a silver thiosulfate mixture on the addition of ammonia solution (Figure 3). Attempts to analyze the UV$-$vis spectroscopic data using SPECFIT and comparing it with literature showed that the species $AgS_2O_3NH_3^-$ or $AgS_2O_3(NH_3)_2^-$ or both could fit the model. But, again as for the potentiometric results, a model containing only $AgS_2O_3NH_3^-$ gave much lower overall standard deviations with a reasonable calculated log $\beta_{111}$ value. This value was found to be about 0.8 log units smaller than that derived potentiometrically (Table 1). Although it is difficult to cite a particular reason for this difference, the difference in the measurement techniques, large errors seen in the spectrophotometric study, and ignorance of changes in the activity of $NH_3$ must all be noted. The calculated spectrum of $AgS_2O_3NH_3^-$ is presented in Figure 4.

**Ag(I) Hydrodynamic Voltammetry.** Two superimposed $i-V$ curves were seen for a solution of Ag(I) (two minimum peaks in the d$i$/d$E$ curves, Figure 5) using a silver rotating disk electrode. This effect was sensitive to the procedure

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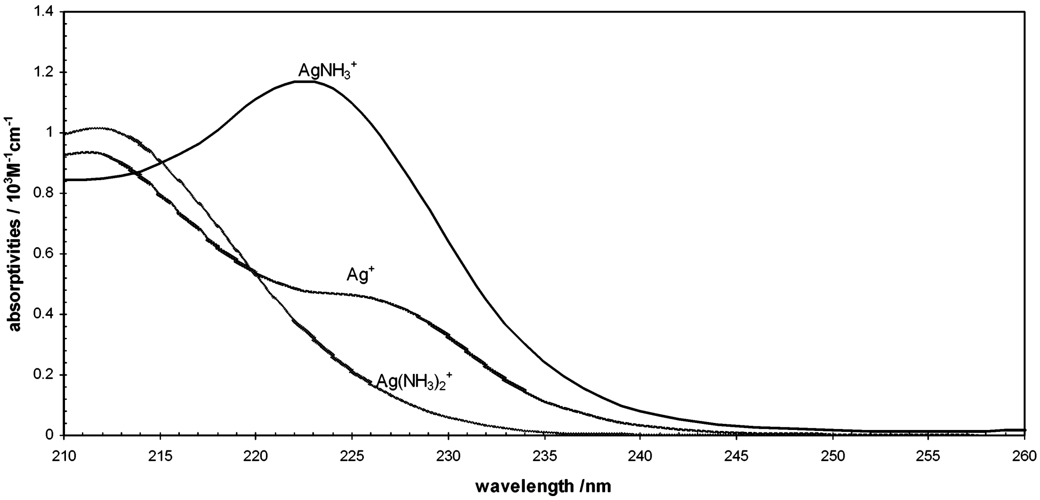

**Figure 2.** Deconvoluted spectra for the various Ag(I)−$NH_3$ species calculated using SPECFIT. Note that $NH_3$(aq) does not absorb in this wavelength range.

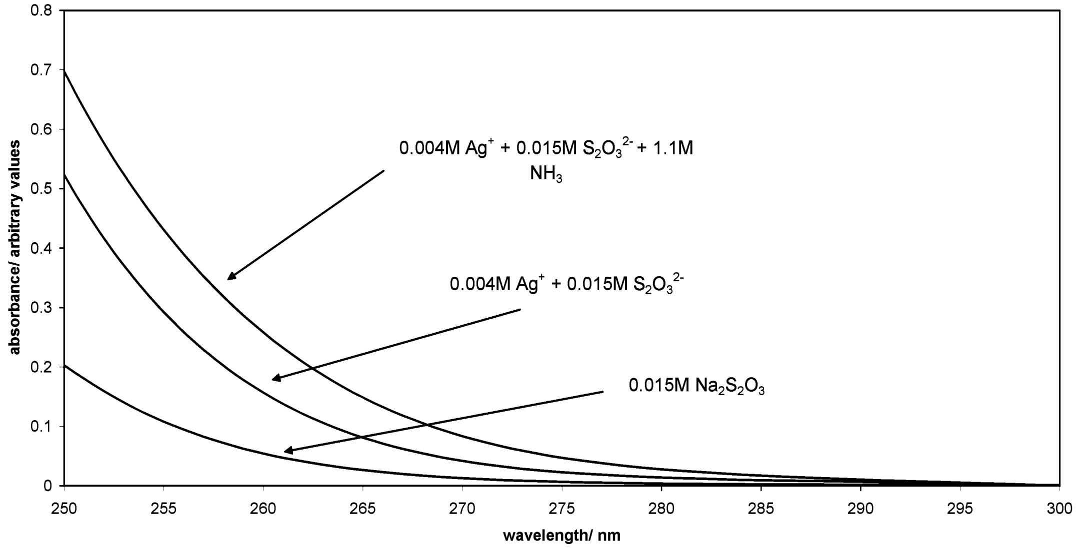

**Figure 3.** Spectra showing the presence of a mixed Ag(I)−$NH_3$−$S_2O_3^{2-}$ species. Note that $NH_3$(aq) and all the Ag(I)−$NH_3$ species do not absorb in this region.

used to prepare and clean the rotating electrode surface. Better results were obtained using a silver plated rotating platinum electrode. Although it gave an unsymmetrical d$i$/d$E$ curve, the analysis implied a reversible process with $n = 1.1$ using eq 10. Graphical analysis of the data based on $E_{1/2}$ versus log[$S_2O_3^{2-}$] (Figure 6) gave stability constants of $AgS_2O_3NH_3^-$ and $Ag(S_2O_3)_2^{3-}$ comparable to those obtained by other methods (Table 1).

**Au(I)−$NH_3$−$S_2O_3^{2-}$ Potentiometry.** Rest potentials recorded during the hydrodynamic voltammetric experiments were generally noisy but showed the stoichiometric presence of $AuS_2O_3NH_3^-$ and $Au(S_2O_3)_2^{3-}$. Data from separate potentiometric experiments using a gold wire at high [$NH_3$(aq)] in the range 6−12 M, conducted either simultaneously with the UV−vis spectrophotmetric experiments or separately, showed similar results and also were able to confirm the presence of the $Au(NH_3)_2^+$ species at a [$NH_3$]/[$S_2O_3^{2-}$] ratio $>10^5$. These experiments, although performed with lower $[Au(I)]_T$ in the range 7−60 $\mu$M, were reproducible and consistent with the spectrophotometric data indicating the increased sensitivity of the gold electrode in the presence of excess $NH_3$.[11] Using graphical methods to analyze the rest potentials and SPECFIT to analyze the other potentiometric data, consistent values of stepwise formation constants were obtained (Table 1).

**Au(I)−$NH_3$−$S_2O_3^{2-}$ UV−Vis Spectrophotometry.** The UV−vis spectrum of $Au(S_2O_3)_2^{3-}$ shown in Figure 2 of a previous report[26] with a value of $\lambda_{max} < 265$ nm is unreliable. It shows spectral transmittance >100% at $\lambda < 265$ nm (Figure 2),[26] indicating instrumentation errors. However, the UV−vis absorption bands for $Au(S_2O_3)_2^{3-}$ (Figure 7) obtained in the present study are consistent with $Ag(S_2O_3)_2^{3-}$ (Figure 4), where only a broad UV absorption band which increases in absorbance with decreasing wavelength <300 nm was observed. Despite the absence of distinct absorbance peaks, changes in UV absorptivity could be used to derive information about changes in speciation.

Only at very low concentrations of $Au(S_2O_3)_2^{3-}$, spectrophotometric changes in the UV region with moderate concentration of $NH_3$(aq) were seen at pH = 12 (compare

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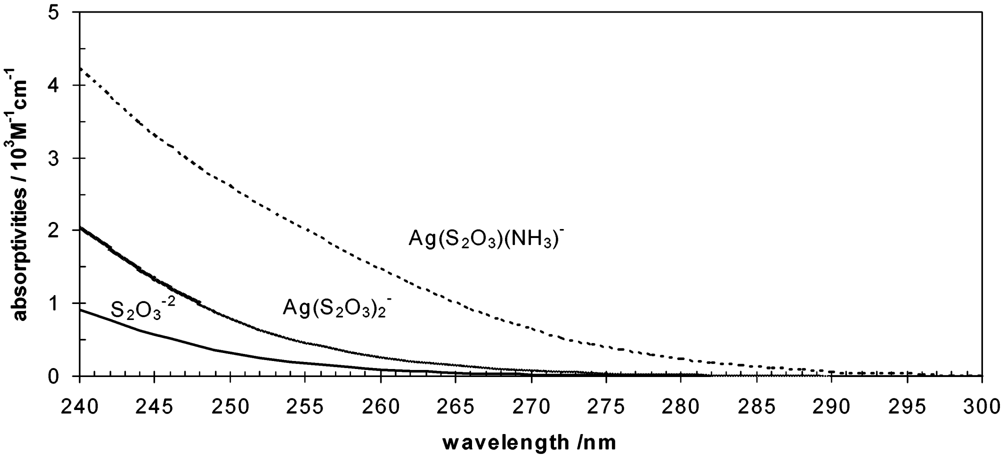

**Figure 4.** Deconvoluted spectra for thiosulfate and the various $Ag(I)-S_2O_3^{2-}-NH_3$ species calculated using SPECFIT.

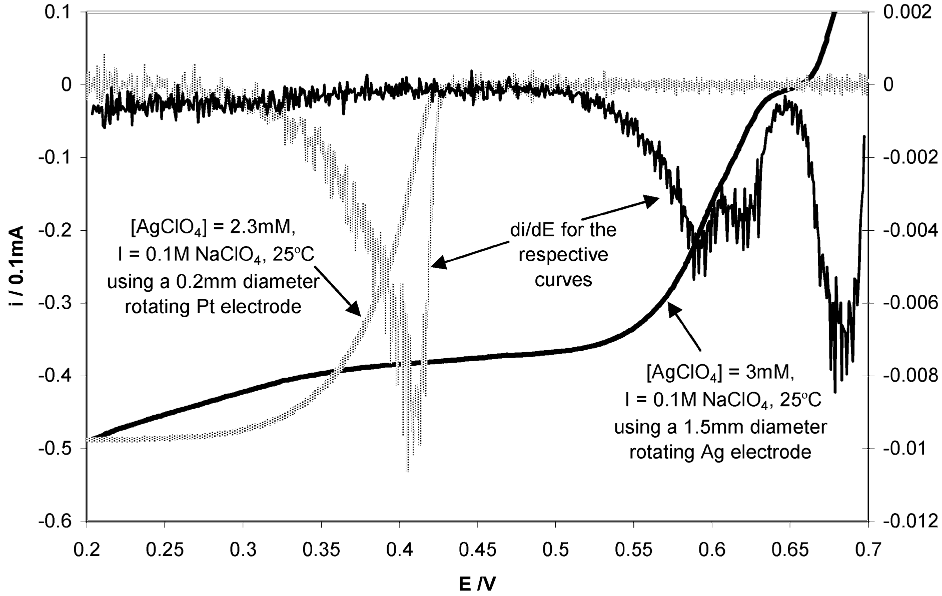

**Figure 5.** Current (*i*)−potential (*E*) curves and the derivatives (d*i*/d*E*) for hydrodynamic voltammetry of Ag(I) solutions

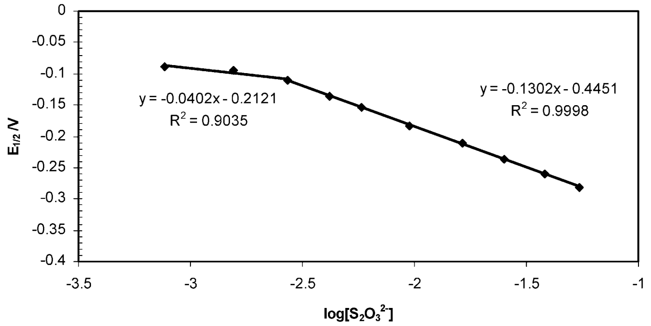

**Figure 6.** Plot of adjusted half-wave potentials of the Ag(I)/Ag(0) reduction process against log[$S_2O_3^{-2}$] for $[Ag(I)]_T$ = 3 mM, 0.8 mM ≤ [$S_2O_3^{-2}$] ≤ 55 mM, with $[NH_3]_T$ = 1.7 M using a 1.5 mm diameter platinum electrode rotating at 1000 rpm.

Figures S3 and S4). These spectral changes were analyzed using SPECFIT with all possible models, and it was found that the inclusion of the species $AuS_2O_3NH_3^-$ in the model along with $Au(S_2O_3)_2^{3-}$ gave the best results with the smallest overall standard deviations for both the spectral fit and variation in the stability constant values (log $K_{111}$ values, Table 1). No significant changes in the $Au(S_2O_3)_2^{3-}$ spectrum were detected with respect to changes in pH (5 to 12), ruling out any interaction between Au(I) and $OH^-$. As with the $Ag(I)-NH_3-S_2O_3^{2-}$ analysis, the spectrum of $S_2O_3^{2-}$ was fixed in the calculations, and the deconvoluted spectra of the various Au(I) species were obtained (Figure 7). The value of log $\beta_{120}$ of $Au(S_2O_3)_2^{3-}$ was fixed at 26.0,[10] and the corresponding log $K_{111}$ value was calculated via

$$\log K_{111} = \log \beta_{111}(AuS_2O_3NH_3^-) - \log \beta_{120}(Au(S_2O_3)_2^{3-}) \quad (14)$$

In experiments with the addition of $NH_3$ in large excess, further spectral changes were observed, and SPECFIT modeling implied the formation of $Au(NH_3)_2^+$. Although larger errors in the derived spectra for this species were seen, the spectral information was similar to the spectrum of the Au(I) species formed by leaching a gold wire in aerated concentrated ammonia (~12 M) solution for 2 weeks at room temperature. As above, the value of log $K_{102}$ of $Au(NH_3)_2^+$ (eq 15) was calculated to be −5.4.

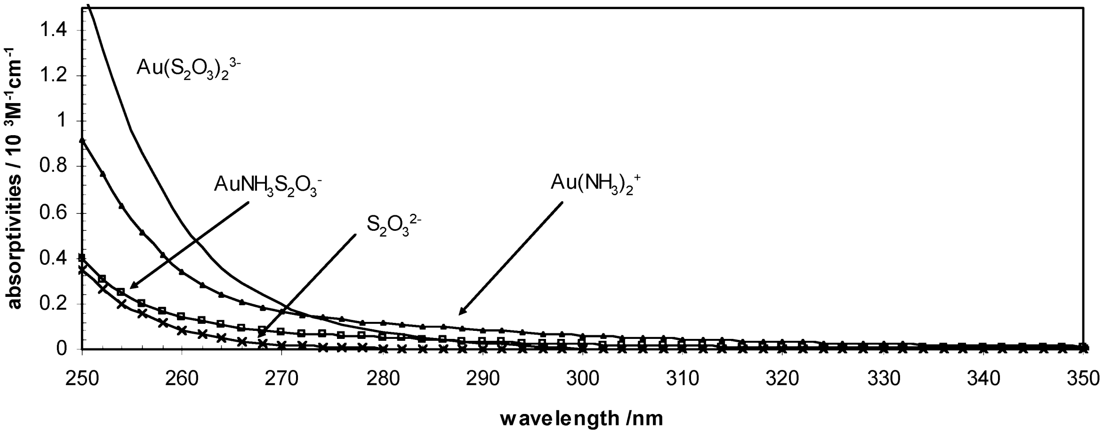

**Figure 7.** Deconvoluted spectra for thiosulfate and the various Au(I) species calculated using SPECFIT.

$$\log K_{102} = \log \beta_{102}(Au(NH_3)_2^+) - \log \beta_{111}(AuS_2O_3NH_3^-) \quad (15)$$

**Au(I) Hydrodynamic Voltammetry.** Independent confirmation of the UV− vis spectrophotometric results at moderately large $[NH_3]/[Au(S_2O_3)_2^{3-}]$ ratios were obtained. The current−potential data obtained as a consequence of the Au(I)/Au(0) reduction process, from linear voltammetric scans at different compositions, were differentiated to obtain the $E_{1/2}$ value as a minimum point value (Figure 8). A reasonable reduction curve for Au(I) (<5 mM of $Au(S_2O_3)_2^{3-}$ and $S_2O_3^{2-}$, Figure 8) was only seen in the presence of high concentration of $NH_3$ or $Cl^-$ (>0.1 M).[9] For example, a solution of 1.5 mM $Au(S_2O_3)_2^{3-}$, 4 mM $S_2O_3^{2-}$ required >0.5 M $NH_3$ to produce a significant minimum peak (Figure 8). The results obtained with total ammonia concentration $[NH_3]_T$ < 1 M were from a reversible process ($n \approx 1$ according to eq 10) but with the limiting current increasing with $[NH_3]_T$ until a maximum value at $[NH_3]_T$ > 1 M (Figure 8). Such results can be rationalized to the presence of a junction resistance between the gold electrode and the bulk solution which is reduced by the presence of an Au−ligand surface species on the electrode.[9,27] With increasing $[NH_3]_T$, a change in the $E_{1/2}$ values of ~0.059 V/log[$NH_3$] was observed with respect to $[NH_3]_T$ indicating the stoichiometric complexation of Au(I) with one bound $NH_3$ molecule (Figure 9). With the addition of $S_2O_3^{2-}$ to solutions of gold(I) thiosulfate containing a large excess of ammonia (Figure 10), the coordination number with respect to $S_2O_3^{2-}$ ions increased from 1 to a maximum of 2. These results were consistent even with different initial $[Au(I)]_T$ implying the formation of mononuclear complexes. Thus, it was concluded that the first complex formed was $AuNH_3S_2O_3^-$ and the change in slope to 0.118 V/log[$S_2O_3^{2-}$] with respect to increasing [$S_2O_3^{2-}$] implied the reformation of $Au(S_2O_3)_2^{3-}$ at high [$S_2O_3^{2-}$] (Figure 10). Using this model, the difference in the *y* intercepts gave the stepwise formation constant value for $AuNH_3S_2O_3^-$ (log $K_{111}$, eq 14) of −3.8 (eqs 12 and 13). No higher order complexes were detected at higher [$S_2O_3^{2-}$] with background KCl ($I$ = 1 M).

## Discussion

Relatively consistent results have been obtained from the various techniques used to analyze the $Ag(I)-S_2O_3^{2-}-NH_3$ and the $Au(I)-S_2O_3^{2-}-NH_3$ systems. The Ag/Ag(I) potentiometry and voltammetry using a rotating disk electrode have confirmed the results based on UV−vis spectrophotometry. Both these techniques have been successfully utilized to confirm the spectrophotometric results of the Au(I)−ammonia−thiosulfate system. With this in mind, it is of interest to note that $AgS_2O_3(NH_3)_2^-$ was not detected in the present study although such a species would be expected according to the previous work by De Marco et al.[8] A possible reason for this difference could be the result of an overestimation in the previous work that may be due to difficulties inherited in analyzing the 3 ligand system ($Ag-NH_3-S_2O_3^{2-}-SCN^-$) examined by DeMarco et al.[8]

Both Au(I) and Ag(I) form linear complexes with $S_2O_3^{2-}$ and $NH_3$,[28,29] and hence, the mixed $S_2O_3^{2-}-NH_3$ complexes of Au(I) and Ag(I) are also expected to be linear. This implies that there should be some similarity between the two systems, and indeed, a correlation is seen when calculating the ratio of stability constants for the mixed complexes,[30] i.e., [(log $\beta_{120}$ − log $\beta_{111}$)/(log $\beta_{120}$ − log $\beta_{102}$)] which is ~0.4 for both Ag(I) and Au(I). With the stability constants of the Cu(I) system known (log $\beta_{102}(Cu(NH_3)_2^+) = 9.92$, 20 °C, $I$ = 0.1 M ($KNO_3$)[31] and log $\beta_{120}(Cu(S_2O_3)_2^{3-}) = 12.27$, 25 °C, $I$ = 1.6 M ($Na_2SO_4$)[32]), a systematic increase in the stability of the $M(I)(S_2O_3)_2^{3-}$ complexes over $M(I)(NH_3)_2^+$ (i.e., log $K_{sys}(M) = \log \beta_{120}(M(S_2O_3)_2^{3-}) - (\log \beta_{102}(M(NH_3)_2^+)$, log $K_{sys}(Cu) = 2.4$, log $K_{sys}(Ag) = 6.1$ and log $K_{sys}(Au) = 9.1$) is seen on going down the IB periodic group from Cu(I) to Au(I). This result is consistent with the theory of increasing softness of the M(I) ions on going from Cu(I) to Au(I) and the greater softness of $S_2O_3^{2-}$ compared to $NH_3$.[33] It explains

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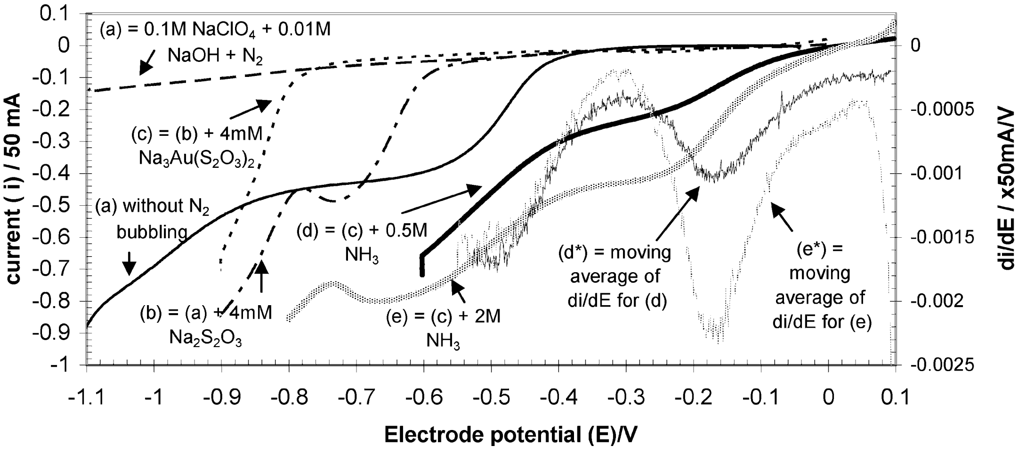

**Figure 8.** Typical current (*i*)−potential (*E*) curves (c, d, and e) and the moving average (20 points) of the derivatives (d*i*/d*E*) for the hydrodynamic voltammetry of Au(I) solutions (d* and e*). Also included are the typical current (*i*) potential (*E*) curves obtained for only 1 M NaClO$_4$ solutions (a) with and without N$_2$ bubbling and (b) with Na$_2$S$_2$O$_3$.

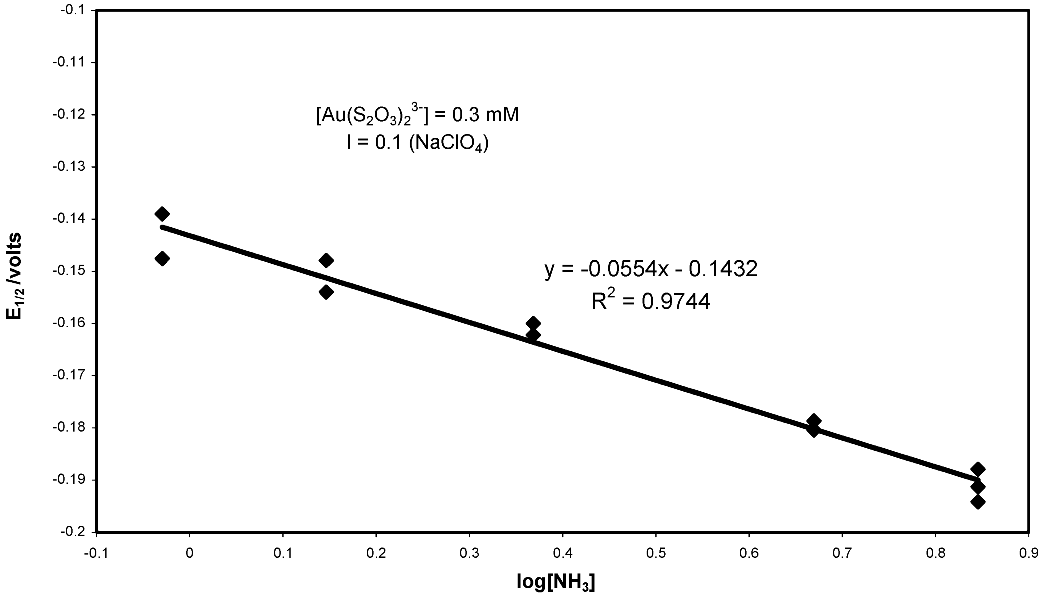

**Figure 9.** Results of the Au(I)−S$_2$O$_3$$^{2-}$−NH$_3$ hydrodyamic voltammetric experiments conducted by measuring the $E_{1/2}$ potential of various Au(S$_2$O$_3$)$_2$$^{3-}$ solutions against [NH$_3$]$_T$ (0.172−7.00 M). Markers are the raw data points while the line is the best linear fit.

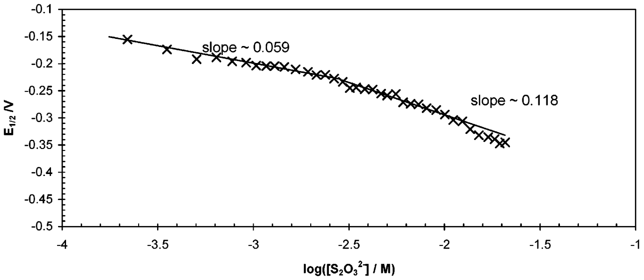

**Figure 10.** Representative plot of half-wave potentials of the Au(I)/Au(0) process from linear voltametric scans of Na$_3$Au(S$_2$O$_3$)$_2$ solutions at fixed [NH$_3$]$_T$ = 5.8 against log[Na$_2$S$_2$O$_3$]$_T$ using a 3 mm diameter gold electrode rotating at 1000 rpm.

why S$_2$O$_3$$^{2-}$ is the preferred fixing agent for silver halide photography[1] and is used in electroplating of these metals.[4] It also explains the large stability of Au(S$_2$O$_3$)$_2$$^{3-}$ making this observation useful in postulating that S$_2$O$_3$$^{2-}$ is also involved in the gold dissolution mechanism in gold extraction with Cu(II)−NH$_3$−S$_2$O$_3$$^{2-}$ reagents, unlike the widely reported mechanism of Au(NH$_3$)$_2$$^+$ formation in the rate determining step.[34] From these results, it can be implied that Au(I) would preferentially complex ligands containing sulfur groups over those with only amino groups suggesting the chemical reason for the pharmacological benefits of using gold(I) salts in medical treatments.[35,36]

## Conclusions

Potentiometry, hydrodynamic voltammetry, and UV−vis spectrophotometry of the Ag(I)−NH$_3$−S$_2$O$_3$$^{2-}$ and the Au(I)−NH$_3$−S$_2$O$_3$$^{2-}$ systems show the similarity between the solution behavior of the Au(I) and Ag(I) systems. In both cases, only one mixed ligand complex, M(I)NH$_3$S$_2$O$_3$$^-$ (M(I) = Ag(I) or Au(I)), appears to be stable. The value of the stability constant of M(I)NH$_3$S$_2$O$_3$$^-$ is intermediate between

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the lower value for $M(I)(NH_3)_2^+$ and the higher for $M(I)(S_2O_3)_2^{3-}$ at 25 °C and $I = 0.1$ M $NaClO_4$.

**Acknowledgment.** The authors thank Prof. M. J. Nicol for his helpful discussions and comments, and Profs. G. Hefter and P. M. May for lending the spectrophotometric equipment and helpful discussions on the ESTER computer program for the calculation of stability constants.The A. J. Parker Cooperative Research Centre for Hydrometallurgy is acknowledged for financial assistance.

**Supporting Information Available:** Figures S1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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