

Electrometric Investigations of the Formation of Uranyl Antimonites and Thioantimonites

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A formação e a composição de antimonitos e tioantimonitos de dioxourânio(VI) obtidos pela interação de ânions antimonitos (SbO_3^{3-} e SbO_2^-) e tioantimonitos (SbS_3^{3-} , $\text{Sb}_2\text{S}_5^{4-}$ e SbO_2^-) com dioxourânio(VI) têm sido investigadas por meio de técnicas eletrométricas envolvendo titulações condutométricas e pH-métricas entre os reagentes. Os pontos finais obtidos a partir de inflexões acentuadas nas curvas de titulações fornecem convincentes evidências sobre a formação e precipitação de orto-antimonito ($3\text{UO}_2\text{O} \cdot \text{Sb}_2\text{O}_3$), orto-tioantimonito ($3\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$), e piro-tioantimonito ($2\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) de dioxourânio(VI) nas vizinhanças do pH 7,0; 7,7 e 5,9, respectivamente. Também foram realizadas investigações analíticas sobre os precipitados obtidos que comprovaram os resultados dos estudos eletrométricos.

The formation and composition of uranyl antimonites and thioantimonites obtained by the interaction of antimonite (SbO_3^{3-} e SbO_2^-) and thioantimonite (SbS_3^{3-} , $\text{Sb}_2\text{S}_5^{4-}$ e SbO_2^-) anions with UO_2^{2+} were investigated by means of electrometric techniques involving pH and conductometric titrations between the reactants. The end points obtained from the sharp inflections and breaks in the titration curves provide cogent evidence for the formation and precipitation of uranyl ortho-antimonite ($3\text{UO}_2\text{O} \cdot \text{Sb}_2\text{O}_3$), ortho-thioantimonite ($3\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$), and pyro-thioantimonite ($2\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) in the neighborhood of pH 7.0, 7.7 and 5.9, respectively. Analytical investigations of the precipitates obtained were also carried out which substantiate the results of the electrometric study.

Keywords: *uranyl antimonites, uranyl thioantimonites, electrometry*

Introduction

Antimony is not used in industry in the unalloyed state to any extent. Its main use in the metallic state is as a constituent of many alloys, to which it imparts certain desired properties, such as expansion upon solidification, increased hardness, and corrosion resistance¹. The electrodeposition of antimony alloys employs antimonites and thioantimonites in alkaline media^{2,3}. The electrodeposits of antimony alloys are generally brittle and stressed and do not adhere well to the base metal. Until now, the baths developed have very few practical applications. The properties of antimony and its low cost could make electrodeposited antimony very useful if a really satisfactory plating bath were developed. The problem in the electrodeposition baths seems to be due to the complicated aqueous solution chemistry of antimony.

The problem in electrodeposition antimony baths, and insufficient data on the chemistry of oxy- and thio-anionic Sb(III) compounds led the author to investigate them. It should also be noted that interest in the chemistry of the ternary antimony compounds has recently been increasing due to their probable use as semiconductors⁴.

The chemistry of antimony is complicated. It has been reported⁵ that investigations on antimony are made difficult by the fact that sometimes it appears as both Sb(III) and Sb(V) in the same compound. The antimony compounds are formally similar, but because of the tendency of antimony to form five or six bonds, the species in an aqueous solution of similar arsenic and antimony compounds may be different⁶.

In earlier publications, the results of different thioanion formations of Sb(III)⁷, As(III)⁸ and W(VI)⁹, and the formation and composition of antimonates and thioantimonates of uranyl¹⁰ and cadmium¹¹ has been reported. In view of

the interesting results obtained, it was considered worthwhile to extend the investigations to the reaction between uranyl and different antimonite¹² and thioantimonite⁷ anions.

Experimental

Merck's guaranteed extra-pure reagents, SbCl_3 , $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, KOH , $\text{UO}_2(\text{NO}_3)_2$ and hydrochloric acid were used, and their solutions were prepared in freshly distilled water. The sodium ortho-thioantimonite, Na_3SbS_3 , solution was prepared by carefully digesting one mole of a synthesized sample of Sb_2S_3 with three moles of Na_2S . The concentration of the stock solution was further checked by determining antimony as sulfide^{13a} and sulfur by the wet process^{13b}. Variations in the pH of the thioantimonite solution were made by the gradual addition of hydrochloric acid⁷. Similarly, potassium ortho-antimonite, K_3SbO_3 , was prepared by digesting a synthesized sample of Sb_2O_3 with the required amount of KOH . Dilute hydrochloric acid was used for variations in the pH of the ortho-antimonite solution¹².

Conductometric and pH measurements were carried out as usual⁹. Twenty-five mL of titre solution was taken in the cell each time and thermostated at $(25.0 \pm 0.1)^\circ\text{C}$. Using different concentrations of the reactants, a series of glass electrode and conductometric titrations was performed. The observed changes in pH were plotted as a function of the volume of the titrant added. The inflections obtained by the curves were confirmed by the pronounced maxima in differential graphs in dpH/dV . The endpoints in conductometric titrations were located graphically. The electrometric titration results on the formation of thioantimonites and antimonites of uranyl are summarized in Table 1. Only three figures are given for the sake of brevity.

The precipitates obtained at the endpoints of the titrations were also analyzed to substantiate the electrometric results. The different uranyl thioantimonites were prepared by mixing stoichiometric amounts of uranyl nitrate solution with the respective sodium thioantimonite solution. Similarly, the uranyl ortho-antimonite was precipitated by the interaction of a uranyl nitrate solution with potassium ortho-antimonite. The precipitates obtained were washed

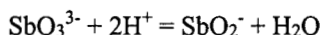
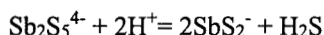
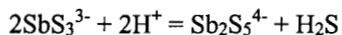
Table 1. Summary of results of electrometric titrations. Volume of titre solution taken in the cell = 25 mL.

Molarity of solutions		Equivalence points (mL)			Formula supported
		Calcd.	Observed from		
			pH	Conductance	
$\text{UO}_2(\text{NO}_3)_2$	Na_3SbS_3	Direct titrations. Fig. 1, curves 1 and 3			
M/20	M/375	2.00	2.00	2.00	$3\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$
M/40	M/800	1.88	1.88	1.87	
M/60	M/1100	2.05	2.04	2.04	
		Reverse titrations. Fig. 1, curves 2 and 4			
M/150	M/20	2.22	2.22	2.20	$3\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$
M/350	M/40	1.90	1.90	1.90	
M/500	M/60	2.00	2.00	2.02	
$\text{UO}_2(\text{NO}_3)_2$	$\text{Na}_4\text{Sb}_2\text{S}_5$	Direct titrations. Fig. 2			
M/20	M/500	2.00	2.00	2.00	$2\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$
M/40	M/900	2.22	2.20	2.20	
M/60	M/1400	2.14	2.14	2.12	
$\text{UO}_2(\text{NO}_3)_2$	K_3SbO_3	Direct titrations. Fig. 3, curves 1 and 3			
M/60	M/1000	2.25	2.25	2.25	$3\text{UO}_2\text{O}\cdot\text{Sb}_2\text{O}_3$
M/80	M/1500	2.00	2.00	2.00	
M/100	M/2000	1.88	1.86	1.85	
		Reverse titrations. Fig. 3, curves 2 and 4			
M/6000	M/1000	2.78	2.80	2.80	$3\text{UO}_2\text{O}\cdot\text{Sb}_2\text{O}_3$
M/8000	M/1500	3.12	3.12	3.10	
M/10000	M/2000	3.33	3.30	3.32	

several times with aqueous ethanolic 10% (v/v) solution and dried completely in a vacuum desiccator. A known amount (2 g) of each of these dried precipitates was digested with conc. HNO_3 (15 mL) until dry in a steam bath. The treatment was repeated two times. The residue was dissolved in a minimum of hydrochloric acid and then antimony was determined as sulfide^{13a} and uranium as oxinate^{13c}. Sulfur in the uranyl thioantimonites was determined gravimetrically by the wet process^{13b}. The results are shown in Table 2.

Results and Discussion

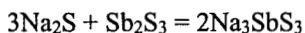
A recent study by the author on the acidification of alkali metal thioantimonites^{7,14} and antimonites¹² shows the existence of three different thioantimonite (SbS_3^{3-} , $\text{Sb}_2\text{S}_5^{4-}$ and SbO_2^-) and two antimonite (SbO_3^{3-} and SbO_2^-) species. The step-by-step formation of these anions by gradual addition of acid may be represented as follows:



The non-existence of $\text{Sb}_2\text{O}_5^{4-}$ corresponding to $\text{Sb}_2\text{S}_5^{4-}$ is in agreement with the results reported by Perrin¹⁵.

Uranyl thioantimonites

The solution of sodium ortho-thioantimonite (pH 11.5) was prepared by digesting an analyzed sample of antimony trisulfide in a sodium sulfide solution of the required strength.



Sodium pyro-thioantimonite (pH 8.9) and meta-thioantimonite (pH 6.8) were prepared by progressive additions of hydrochloric acid to sodium ortho-thioantimonite solutions in the molar ratios 1:1 and 2:1, respectively.

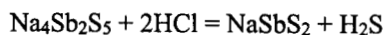
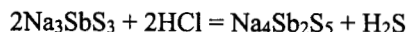


Figure 1 illustrates the curves of the pH and conductometric titrations performed between the solutions of sodium ortho-thioantimonite and uranyl nitrate. In the direct pH titrations (curve 1), when uranyl nitrate solution (pH

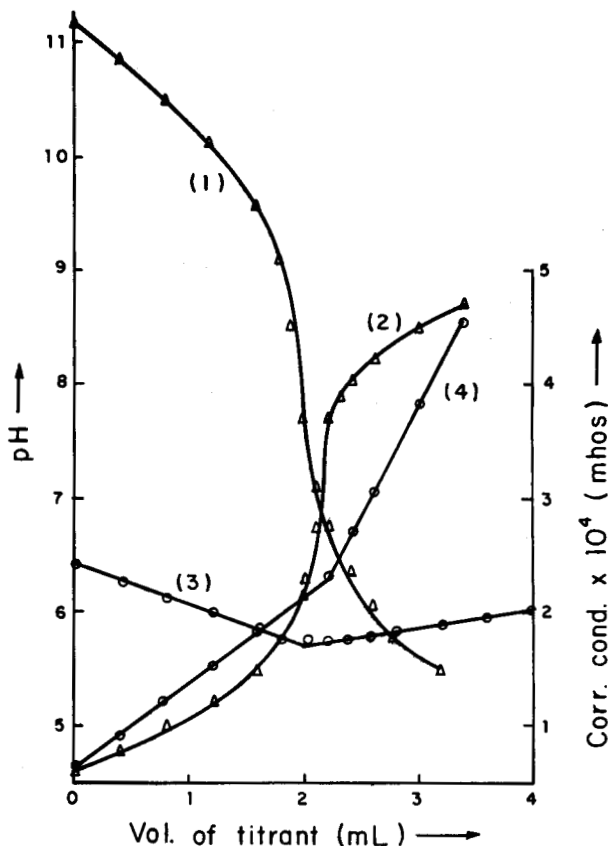


Figure 1. pH(1,2) and conductometric (3,4) titrations of ortho-thioantimonite. 1 and 3: M/20 $\text{UO}_2(\text{NO}_3)_2$ added to 25 mL of M/375 Na_3SbS_3 . 2 and 4: M/20 Na_3SbS_3 added to 25 mL of M/150 $\text{UO}_2(\text{NO}_3)_2$.

Table 2. Summary of analytical results of the precipitates.

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (Calculated)		
		U	Sb	S
Analysis of the ortho-thioantimonite precipitates				
$3\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$	Direct*	57.37 (57.31)	19.51 (19.54)	15.42 (15.44)
	Reverse*	57.28	19.58	15.47
Analysis of the pyro-thioantimonite precipitate				
$2\text{UO}_2\text{S} \cdot \text{Sb}_2\text{S}_3$	Direct	50.48 (50.44)	25.76 (25.80)	16.96 (16.98)
Analysis of the ortho-antimonite precipitates				
$3\text{UO}_2\text{O} \cdot \text{Sb}_2\text{O}_3$	Direct	62.19 (62.12)	21.13 (21.18)	-
	Reverse	62.10	21.22	-

*Direct: uranyl nitrate solution added to sodium ortho-thioantimonite solution.

*Reverse: sodium ortho-thioantimonite solution added to uranyl nitrate solution.

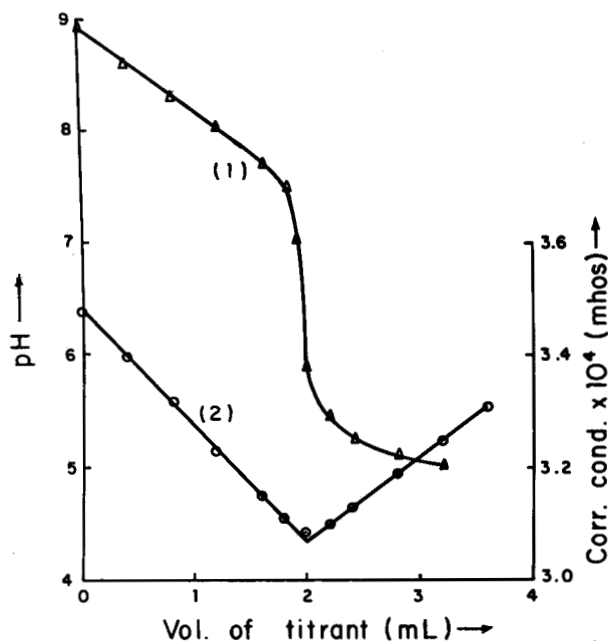
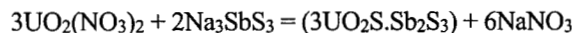


Figure 2. pH (1) and conductometric (2) titrations of pyro-thioantimonite. $M/20 \text{ UO}_2(\text{NO}_3)_2$ added to 25 mL of $M/500 \text{ Na}_4\text{Sb}_2\text{S}_5$.

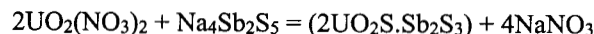
4.1) was added from the microburette to the alkali ortho-thioantimonite solution (pH 11.5), a sharp fall in pH was noted with an inflection at the molar ratio of $\text{UO}_2^{2+}:\text{SbO}_3^{3-}$ as 3:2 in the vicinity of pH 7.7, corresponding to the stoichiometry for the formation of uranyl ortho-thioantimonite, $3\text{UO}_2\text{S}\cdot 2\text{Sb}_2\text{S}_3$. In reverse titrations (curve 2), when Na_3SbS_3 solution was added to the uranyl nitrate solution, the pH first increased very slowly, but at the end-point it made a jump corresponding to the formation of the same compound in accordance with the following equation.



Employing similar concentrations of the reactants, both direct (curve 3) and reverse (curve 4) conductometric titrations between uranyl nitrate and sodium ortho-thioantimonite gave well-defined breaks at the 3:2 molar ratio of $\text{UO}_2^{2+}:\text{SbS}_3^{3-}$, confirming the formation of uranyl ortho-thioantimonite. In direct titrations, when uranyl nitrate solution was added from the microburette to the solution of alkali ortho-thioantimonite, a decrease in conductance was observed (due to the removal of the SbS_3^{3-} ion in the form of a precipitate) until the stoichiometric endpoint, after which conductance increased with the increase in ionic concentration. In the case of reverse titrations, as comparatively more mobile sodium ions are introduced in the cell, the conductance values show a gradual increase from the very beginning of the titration.

Figure 2 illustrates the changes occurring in the pH and conductance values when uranyl nitrate solution is added to sodium pyro-thioantimonite solution. The titration

curves provide well-defined inflections and breaks at the point where the molar ratio of $\text{UO}_2^{2+}:\text{Sb}_2\text{S}_4^{5-}$ is 2:1, which corresponds to the stoichiometry for the formation of $2\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ in the neighborhood of pH 5.9 (Table 1). The reaction can be represented by the following equation:



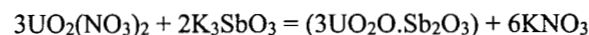
The pyro-thioantimonite, $2\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, has been found to be very soluble in an excess of the reagents, particularly in uranyl nitrate and hence reverse titrations could not be carried out. For similar reasons all the pyro-thioantimonite titrations were performed in the presence of 20% ethanol.

Investigations of the reaction of uranyl nitrate with sodium meta-thioantimonite failed to give any reliable results. This may be ascribed to the soluble nature of the product, to the small difference in pH values of the reactants, and to the presence of sodium chloride in appreciable amounts preventing the occurrence of a break in the titration curves.

Uranyl antimonites

The solution of potassium ortho-antimonite (pH 11.2) was prepared by carefully digesting a synthesized sample of Sb_2O_3 in a solution of KOH.

The pH and conductometric investigations of the reaction between the uranyl nitrate and potassium ortho-antimonite solutions are illustrated in Fig. 3. An examination of the results of these titrations reveals that the reaction can be successfully followed by using either of the reactants as titrant (Table 1). In the direct pH titrations (curve 1), when uranyl nitrate solution (pH 4.1) was added from the microburette to the K_3SbO_3 solution (pH 11.2) in the cell, the pH of the latter showed a gradual decrease with a marked downward jump in pH at the stoichiometric endpoint, which corresponds to the formation and precipitation of uranyl ortho-antimonite, $3\text{UO}_2\text{O}\cdot\text{Sb}_2\text{O}_3$, in the vicinity of pH 7.0. In the case of inverse titrations (curve 2), when K_3SbO_3 solution was used as titrant, a sharp upward jump in pH was observed at the 3:2 molar ratio of $\text{UO}_2^{2+}:\text{SbO}_3^{3-}$, confirming the formation of the same compound, uranyl ortho-antimonite, according to the following equation:



Conductometric titrations between uranyl nitrate and potassium meta-antimonite failed to give any reliable results. This may be due to reasons similar to those acting in the case of the thio compound. The formation of uranyl pyro-antimonite, similar to that formed by Sb(V)^{10} , was not indicated in this study.

The precipitates obtained at the endpoints of the titrations of uranyl nitrate with the antimonite and thioantimonite anions were analyzed by classical methods. The results obtained (Table 2) confirm those obtained by the

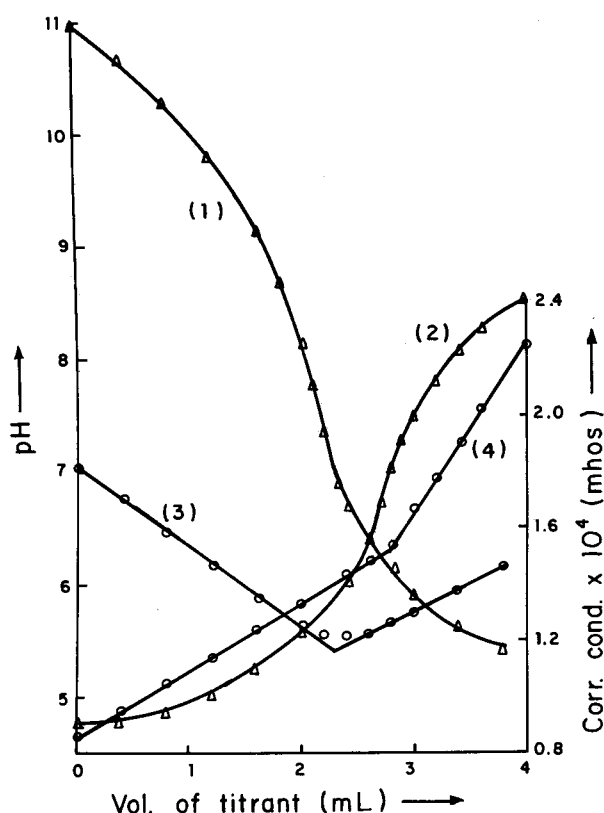


Figure 3. pH (1,2) and conductometric titrations of ortho-antimonite. 1 and 3: M/60 $\text{UO}_2(\text{NO}_3)_2$ added to 25 mL of M/1000 K_3SbO_3 . 2 and 4: M/1000 K_3SbO_3 added to 25 mL of M/6000 $\text{UO}_2(\text{NO}_3)_2$.

electrometric study. The analytical results were also confirmed by atomic absorption spectroscopy.

The present electrometric and analytical investigations confirm the formation and precipitation of uranyl ortho- $3\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ and pyro- $2\text{UO}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ thioantimonites and uranyl ortho-antimonite $3\text{UO}_2\text{O}\cdot\text{Sb}_2\text{O}_3$, in the neighborhood of pH 7.7, 5.9 and 7.0, respectively¹⁶. As the structure of these compounds is not known, they are represented as double oxides, as is usual for such compounds^{17,18}.

Acknowledgments

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