

## Reaction of thorium nitrate with sodium thioarsenate as a function of pH

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The stoichiometries of the compounds formed by the interaction of thorium nitrate and sodium orthothioarsenate/pyrothioarsenate have been established as  $3\text{ThS}_2 \cdot 2\text{As}_2\text{S}_5$  and  $\text{ThS}_2 \cdot \text{As}_2\text{S}_5$  employing pH and conductometric titrations. Formation of these compounds is supported by analytical determinations.

Results on thioanion formation of  $\text{As(III)}^1$  and  $\text{As(V)}^2$  and on the formation and composition of nickel thioarsenates<sup>3</sup> and cobalt thioarsenates<sup>4</sup> were reported by the author earlier. In view of the interesting results obtained, it was considered worthwhile to extend similar investigations on the formation of thorium thioarsenates.

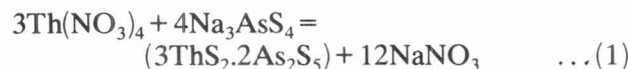
Hydrochloric acid,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  of extra-pure grade were used. Solution of sodium orthothioarsenate was prepared by dissolving  $\text{As}_2\text{S}_5$  in a solution containing requisite amount of sodium sulphide and standardized by determining  $\text{As(V)}$  as magnesium pyroarsenate<sup>5a</sup> and sulphur as  $\text{BaSO}_4$  by wet process<sup>5b</sup>. Calculated amounts of hydrochloric acid were added to  $\text{Na}_3\text{AsS}_4$  solutions in definite proportions to vary the pH (ref. 2).

pH and conductance measurements were carried out as described earlier<sup>3</sup>. Titre solution (25 ml) was taken in the titration cell which was kept at  $25 \pm 0.1^\circ\text{C}$ . Using different concentrations of the reactants a series of pH and conductometric titrations were performed both by direct and reverse methods. Solutions of identical strengths were employed in all titrations for comparison.

The pH of the solution of sodium orthothioarsenate, prepared by dissolving  $\text{As}_2\text{S}_5$  in  $\text{Na}_2\text{S}$  solution in molar ratio 1:3, was found to be 11.3. The pH was varied by the addition of hydrochloric acid. When HCl was mixed with  $\text{Na}_3\text{AsS}_4$  in the molar ratio 1:1 the compound formed was  $\text{Na}_4\text{As}_2\text{S}_7$  (sodium pyrothioarsenate) and the pH of the solution was found to be 8.1.

### Orthothioarsenate titrations

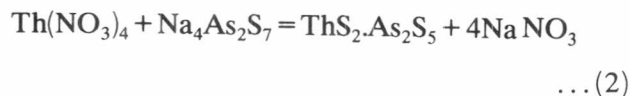
In direct titrations when thorium nitrate solution (pH 2.2) was added to  $\text{Na}_3\text{AsS}_4$  solution (pH 11.3), a sharp fall in pH was noted with an inflection corresponding to the molar ratio of  $\text{Th}^{4+} : \text{AsS}_4^{3-}$  as 3:4, in the vicinity of pH 6.3, suggesting the formation of  $3\text{ThS}_2 \cdot 2\text{As}_2\text{S}_5$ . In reverse titration when  $\text{Na}_3\text{AsS}_4$  solution (pH 11.3) was added to thorium nitrate (pH 2.2), the pH first increased slowly but at the end-point a marked upward jump in pH was observed corresponding to the formation of same compound in accordance with Eq. (1).



Employing similar concentrations of the reactants, both direct and reverse, conductometric titrations between thorium nitrate and alkali orthothioarsenate gave well-defined breaks at 3:4 molar ratio of  $\text{Th}^{4+} : \text{AsS}_4^{3-}$ , confirming the formation of thorium orthothioarsenate. In these titrations conductance values remained almost constant till the stoichiometric end-point was reached, at which a sharp increase in conductance was noticed indicating completion of the precipitation reaction.

### Pyrothioarsenate titrations

The slope and nature of pH and conductometric titrations of sodium pyrothioarsenate (pH 8.1) with thorium nitrate (pH 2.2) were similar to those of the orthothioarsenate. The curves provided well-defined inflections at molar ratio of 1:1 ( $\text{Th}^{4+} : \text{As}_2\text{S}_7^{4-}$ ) suggesting the formation of  $\text{ThS}_2 \cdot \text{As}_2\text{S}_5$  around pH 4.6. The reaction can be represented by Eq. (2).



Since thorium pyrothioarsenate is highly soluble in excess of thorium nitrate, reverse titrations could not give dependable results.

It is noted that after each addition of the titrant it takes a little time for pH and conductance values to become steady. A thorough stirring in the vicinity of equivalence point has a favourable effect. The presence of ethanol slightly improves the position of the end-point and increases the magnitude of the jump in pH curves as it decreases the solubility of the precipitates formed and minimises hydrolysis and adsorption.

The electrometric results are also substantiated by analytical investigations.

The present electrometric, and analytical investigations confirm the formation and precipitation of  $3\text{ThS}_2 \cdot 2\text{As}_2\text{S}_5$  and  $\text{ThS}_2 \cdot \text{As}_2\text{S}_5$  in the neighbourhood of pH 6.3 and 4.6 respectively.

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## References

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