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Reaction of thorium nitrate with sodium thioarsenate as a function of *p*H

Shiva Prasad

Departmento de Engenharia Quimica, Centro de Ciências e Tecnologia, Universidade Federal da Paraiba, Campina Grande, Brazil

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The stoichiometries of the compounds formed by the interaction of thorium nitrate and sodium orthothioarsenate/pyrothioarsenate have been established as $3ThS_2.2As_2S_5$ and $ThS_2.As_2S_5$ employing *p*H and conductometric titrations. Formation of these compounds is supported by analytical determinations.

Results on thioanion formation of As(III)[1] and As(V)[2] and on the formation and composition of nickel thioarsenates[3] and cobalt thioarsenates[4] 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, $Na_2HAsO_4.7H_2O$, $Na_2S.9H_2O$ and $Th(NO_3)_4.5H_2O$ of extra-pure grade were used. Solution of sodium orthothioarsenate was prepared by dissolving As_2S_5 in a solution containing requisite amount of sodium sulphide and standardized by determining As(V) as magnesium pyroarsenate[5a] and sulphur as $BaSO_4$ by wet process[5b]. Calculated amounts of hydrochloric acid were added to Na_3AsS_4 solutions in definite proportions to vary the *p*H (ref. 2).

*p*H and conductance measurements were carried out as described earlier[3]. Titre solution (25 ml) was taken in the titration cell which was kept at 25 ± 0.1°C. Using different concentrations of the reactants a series of *p*H and conductometric titrations were performed both by direct and reverse methods. Solutions of identical strengths were employed in all titrations for comparison.

The *p*H of the solution of sodium orthothioarsenate, prepared by dissolving As_2S_5 in Na_2S solution in molar ratio 1:3, was found to be 11.3. The *p*H was varied by the addition of hydrochloric acid. When HCl was mixed with Na_3AsS_4 in the molar ratio 1:1 the compound formed was $Na_4As_2S_7$ (sodium pyrothioarsenate) and the *p*H of the solution was found to be 8.1.

Orthothioarsenate titrations

In direct titrations when thorium nitrate solution (*p*H 2.2) was added to Na_3AsS_4 solution (*p*H 11.3), a sharp fall in *p*H was noted with an inflection corresponding to the molar ratio of Th^{4+}: AsS_4^{3-} as 3:4, in the vicinity of *p*H 6.3, suggesting the formation of $3ThS_2.2As_2S_5$. In reverse titration when Na_3AsS_4 solution (*p*H 11.3) was added to thorium nitrate (*p*H 2.2), the *p*H first increased slowly but at the end-point a marked upward jump in *p*H was observed corresponding to the formation of same compound in accordance with Eq. (1).

$$3Th(NO_3)_4 + 4Na_3AsS_4 = (3ThS_2.2As_2S_5) + 12NaNO_3 \quad \ldots(1)$$

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 Th^{4+}: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 *p*H and conductometric titrations of sodium pyrothioarsenate (*p*H 8.1) with thorium nitrate (*p*H 2.2) were similar to those of the orthothioarsenate. The curves provided well-defined inflections at molar ratio of 1:1 (Th^{4+}:$As_2S_7^{4-}$) suggesting the formation of $ThS_2.As_2S_5$ around *p*H 4.6. The reaction can be represented by Eq. (2).

$$Th(NO_3)_4 + Na_4As_2S_7 = ThS_2.As_2S_5 + 4NaNO_3 \quad \ldots(2)$$

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 *p*H 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 *p*H 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 $3ThS_2.2As_2S_5$ and $ThS_2.As_2S_5$ in the neighbourhood of *p*H 6.3 and 4.6 respectively.

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