FORMATION OF CADMIUM ANTIMONATES AND THIOANTIMONATES: AN ELECTROMETRIC STUDY

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The stoichiometry of the interaction of antimonate (SbO_4^{3-}, $Sb_2O_7^{4-}$, SbO_3^-) and thioantimonate (SbS_4^{3-}) anions with Cd^{2+} have been investigated by employing electrometric techniques involving pH and conductometric titrations between the reactants. The well defined breaks and inflections obtained in the titration curves evidence the formation of cadmium ortho-antimonate ($3CdO.Sb_2O_5$), pyro-antimonate ($2CdO.Sb_2O_5$) and ortho-thioantimonate ($3CdS.Sb_2S_5$) in the vicinity of pH 9.9, 6.2 and 6.8 respectively. Analytical investigations of the compounds have also been carried out which substantiate the results of the electrometric study.

INTRODUCTION

A survey of literature reveals that the chemistry of antimonates and thioantimonates is complicated and no finality seems to have been reached about their constitution[1-5]. A recent study by the author on acidification of alkali metal antimonates[6] and thioantimonates[7] shows the existence of three different antimonate species viz. Sbo_4^{3-}, $Sb_2O_7^{4-}$, Sbo_3^- and olnly one thioantimonate, SbS_4^{3-}. In view of the interesting results obtained, it was considered worthwhile to investigate precisely the composition of cadmium antimonates and thioantimonates obtained by the action of Cd^{2+} with antimonate and thioantimonate anions at different pH levels by means of electroanalytical techniques which have provides more conclusive evidences on the composition of such and allied compounds[6-10]. There is, however, no any reference available in the literature on the formation of cadmium antimonates and thioantimonates.

EXPERIMENTAL

Hydrochloric acid, $KSb(OH)_6$, KOH, $Na_3SbS_4 . 9H_2O$ and $3CdSO_4 . 8H_2O$ used were of extra-pure grade. Their solutions were prepared in carbonate-free distilled water. The solution of potassium ortho-antimonate was prepared by digesting carefully to dryness one mole of $KSb(OH)_6$ in boiling solution of KOH containing two moles of it (Eq. 1)[6].

$$2KOH + KSb(OH)_6 = K_3SbO_4 + 4H_2O \quad (1)$$

The concentration of the potassium ortho-antimonate was further checked by determining the antimony content volumetrically.[11a] The potassium pyro-antimonate and meta-antimonate solutions were prepared[6] by progressive addition of HCl to a solution of K_3SbO_4 in the molar ratio 1 : 1 and 1 : 2, respectively (Eq. 2 and 3).

$$2HCl + 2K_3SbO_4 = K_4Sb_2O_7 + 2KCl + H_2O \quad (2)$$

$$2HCl + K_4Sb_2O_7 = 2KSbO_3 + 2KCl + H_2O \quad (3)$$

pH and conductometric measurements were carried out as described earlier[8]. 25ml of titre solution was taken in the cell each time and thermostated at (25±0.1) °C. Using different concentrations of the reactants, a series of pH and conductometric titrations were performed both by direct and reverse methods, i.e. when cadmium sulphate solution from the microburette was added to the alkali antimonate solution and vice-versa. Similar concentrations of solutions were employed in both the techniques for comparison of results, which are given in Table 1. Only three figures are shown for brevity.

The precipitates obtained at the end-points were also analysed to substantiate the electrometric results. The different cadmium antimonates were prepared by mixing stoichiometric amounts of cadmium sulphate solution with the respective potassium antimonate solutions. Similarly the cadmium ortho-thioantimonate was precipitated by interaction of cadmium sulphate with sodium ortho-thioantimonate. The precipitates obtained were washed several times with aqueous ethanolic solution and dried completely in vacuum desiccator. A known amount of the dried precipitate of orthothioantimonate was digested with excess of HNO_3 to dryness on a steam bath. The treatment was repeated two times to eliminate sulphur. The dried residues were dissolved in minimum quantity of HCl and then antimony was determined volumetrically[11a] and cadmium as pyrophosphate.[11b] Sulphur in the cadmium ortho-thioantimonate was determined gravimetrically by wet process.[11c] The analytical results are given in Table 2.

RESULTS AND DISCUSSION

Cadmium Antimonates:

The pH values of the solutions of cadmium sulphate, potassium ortho-, pyro-and meta-antimonates, as measured by the combined glass electrode, were found to be in the vicinity of 5.7, 11.5, 8.2 and 4.7, respectively.

Ortho-antimonate titrations:

Fig. 1 illustrates the changes occurring in pH and conductance values during the titrations performed between the solutions of cadmium sulphate and potassium ortho-antimonate. In the case of direct pH titrations (curve 1), when the cadmium sulphate solution was added from microburette to the potassium ortho-antimonate solution a gradual decrease in pH

was observed till the stoichiometric end-point is reached and after which the smallest addition of the titrant causes a sharp fall in pH indicating the completion of reaction and suggesting the formation of cadmium ortho-antimonate in the neighbourhood pH 7.9. In the case of reverse titrations (curve 3) the first addition of alkali ortho-antimonate (pH 11.5) to cadmium sulphate solution (pH 5.7) causes an initial decrease in pH till about half the volume of titrant required for the precipitation of cadmium ortho antimonate, is added. This initial lowering in pH value is due to the presence of hydrolysed acid from the cadmium salt. Later on, with the progress of the reaction, pH begins to rise and pronounced upward inflection is obtained at the stoichiometric end-point, corresponding to the molar ratio of Cd^{2+} : SbO_4^{3-} as 3 : 2, confirming the formation of the same compound accordig to Eq. (4).

$$3CdSO_4 + 2K_3SbO_4 = (3CdO \cdot Sb_2O_5) + 3K_2SO_4 \quad (4)$$

Employing similar concentrations of the reactants, both the direct (curve 2) and reverse (curve 4) conductometric titrations were also carried out. The titration curves yield well-defined breaks at the stoichiometric end-point corresponding to the reacting ratio of Cd^{2+} : SbO_4^{3-} as 3 : 2 and conform the formation of the identical compound $3CdO \cdot Sb_2O_5$. In direct titrations, when cadmium sulphate solution was added as titrant to the solution of potassium ortho-antimonate, a decrease in conductance was obtained (due to removal of SbO_4^{3-} ion in the form of precipitate) till the stoichiometric end-point after which conductance increased with the increase in ionic concentration. In case of the reverse titrations, as comparatively more mobile ions are introduced in the cell, the conductance values show a gradual increase from the very beginning of the titration with a brisk increase from the point of completion of the precipitation reaction.

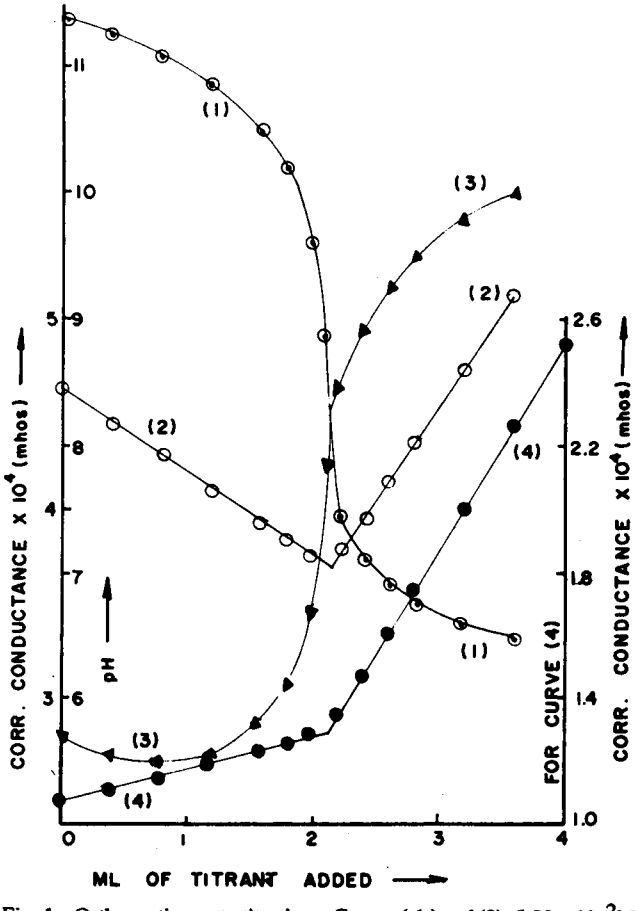

Fig. 1 – Ortho-antimonate titrations. Curves (1) and (2): 5.00 x 10^{-2}M $CdSO_4$ added to 25 ml of 2.86 x 10^{-3}M K_3SbO_4; curves (3) and (4): 1.00 x 10^{-2}M K_3SbO_4 added to 25 ml of 1.25 x 10^{-3}M $CdSO_4$.

Pyro-antimonate titrations:

The changes occurring in pH and conductometric values during the titrations of potassium pyro-antimonate with cadmium sulphate solution are shown in Fig. 2. The pH (curve 1) and conductometric (curve 2) titration curves are similar to those of direct ortho-antimonate titration curves with the inflection corresponding to the molar ratio of Cd^{2+} : $Sb_2O_7^{4-}$ as 2 : 1, suggesting the formation of cadmium pyro-antimonate, $2CdO \cdot Sb_2O_5$ in the vicinity of pH 6 . 2. The reaction can be represented by Eq. (5).

$$2CdSO_4 + K_4Sb_2O_7 = (2CdO \cdot Sb_2O_5) + 2K_2SO_4 \quad (5)$$

The pyro-antimonate, $2CdO \cdot Sb_2O_5$, has been found to be considerably soluble in excess of the reagents particularly in cadmium sulphate and hence reverse titrations could not be carried out. For similar reasons all the pyro-antimonate titrations were performed in presence of 40% ethanol.

Investigations on the reaction of cadmium sulphate with the alkali meta-antimonate failed to give any dependable results. This may be ascribed to the soluble nature of the product, the small diference in pH values of the reactants and the presence of potassium chloride in appreciable amounts preventing the occurrence of breaks in the titration curves.

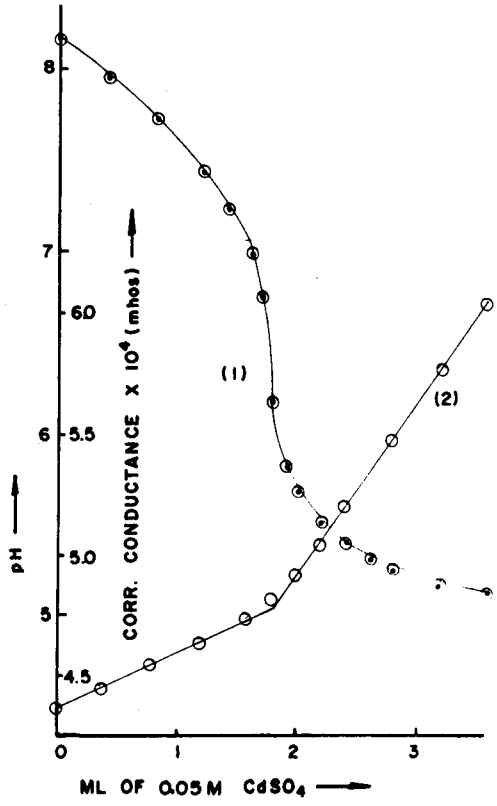

Fig. 2 – Pyro-antimonate titrations. Curves (1) and (2): 5.00 x 10^{-2}M $CdSO_4$ added to 25 ml of 1.82 x 10^{-3}M $K_4Sb_2O_7$.

Table 1: Summary of results of the electrometric titration.
Volume of titre solution taken in the cell = 25 ml.

Concentration of solutions		Equivalence points (ml)			Formula
		Calc.	Observed from		supported
X 10^3M	X 10^3M		pH	conductance	
$CdSO_4$	K_3SbO_4	Direct titrations. Fig. 1, curves 1 and 2.			
50.00	2.86	2.14	2.15	2.15	$3CdO . Sb_2O_5$
25.00	1.67	2.50	2.50	2.50	
16.67	1.00	2.25	2.25	2.20	
		Reverse titrations. Fig. 1, curves 3 and 4.			
1.25	10.00	2.08	2.10	2.10	$3CdO . Sb_2O_5$
1.00	6.67	2.50	2.50	2.50	
0.67	5.00	2.22	2.25	2.25	
$CdSO_4$	$K_4Sb_2O_7$	Direct titrations. Fig. 2			
50.00	1.82	1.82	1.80	1.80	$2CdO . Sb_2O_5$
25.00	1.00	2.00	2.00	2.00	
16.67	0.71	2.14	2.15	2.10	
$CdSO_4$	Na_3SbS_4	Direct titrations. Fig. 3, curves 1 and 2.			
50.00	2.86	2.14	2.15	2.15	$3CdS . Sb_2S_5$
25.00	1.33	2.00	2.00	2.00	
16.67	1.00	2.25	2.25	2.20	
		Reverse titrations. Fig. 3, curve 3 and 4.			
1.25	10.00	2.08	2.10	2.10	$3CdS . Sb_2S_5$
0.91	6.67	2.27	2.30	2.30	
0.71	5.00	2.38	2.40	2.35	

Table 2: Summary of the analytical results.

Proposed formula of the compound	Mode of synthesis	Analysis %: Found (calculated)		
		Cd	Sb	S
Analysis of the ortho-thioantimonate precipitate				
$3CdS . Sb_2S_5$	Direct*	40.23 (40.28)	29.11 (29.08)	30.66 (30.64)
$3CdS . Sb_2S_5$	Reverse*	40.30	29.06	30.63
Analysis of the ortho-antimonate precipitate				
$3CdO . Sb_2O_5$	Direct	47.54 (47.58)	34.38 (34.36)	–
$3CdO . Sb_2O_5$	Reverse	47.60	34.37	–
Analysis of the pyro-antimonate precipitate				
$2CdO . Sb_2O_5$	Direct	38.70 (38.74)	41.99 (41.96)	–
$2CdO . Sb_2O_5$	Reverse	38.77	41.92	–

* Direct – Cadmium sulphate solution added to potassium ortho-thioantimonate solution.
* Reverse – Potassium ortho-thioantimonate solution added to cadmium sulphate solution.

Cadmium Ortho-thioantimonate:

Using different concentrations of cadmium sulphate and sodium ortho-thioantimonate solutions a series of pH and conductometric titrations were performed (fig. 3). Examination of the results of these titrations reveals that the reaction can be sucessfully followed by either of the reactants as titrant (Table 1). The slope and nature of the pH and conductometric titration curves between sodium ortho-thioantimonate (pH 9.8) and cadmium sulphate (pH 5.7) are similar to those of the orthoantimonate. The curves provide well defined inflections at molar ratio of 3 : 2 of Cd^{2+} : SbS_4^{3-} suggesting the formation of $3CdS \cdot Sb_2S_5$ around pH 6.8 according to the Eq. (6).

$$3CdSO_4 + 2Na_3SbS_4 = (3CdS \cdot Sb_2S_5) + 3Na_2SO_4 \quad (6)$$

The presence of ethanol in pyro-antimonate titrations slightly improves the end-points and gives better results as it reduces the solubility of the precipitates as well as hydrolysis. It was noted that after each addition of the reagent it takes a short time for pH and conductance values to become steady. Thorough stirring in the vicinity of the end-point has a favourable effect. Each titration takes about half an hour for completion.

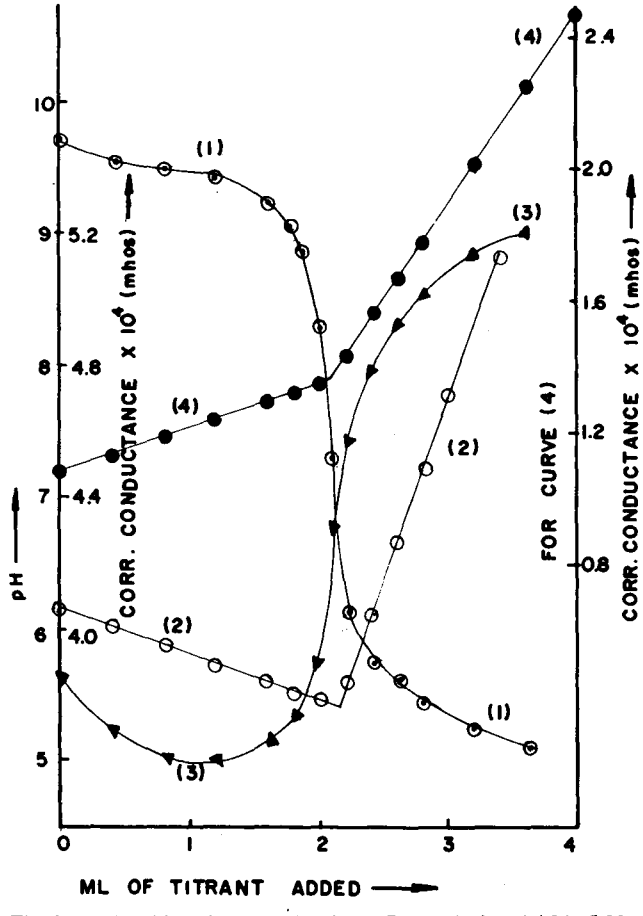

Fig. 3 – Ortho-thioantimonate titrations. Curves (1) and (2): 5.00 x 10^{-2}M $CdSO_4$ added to 25 ml of 2.86 x 10^{-3}M K_3SbS_4; curves (3) and (4): 1.00 x 10^{-2}M K_3SbS_4 added to 25 ml of 1.25 x 10^{-3} $CdSO_4$.

Analytical Results:

The results of the quantitative elemental analysis of the precipitates were used to calculate the proportions of the elements present in the compounds. From these proportions, the composition of the compounds were established which were found to be same as obtained by the electrometric techniques (see Table 2).

The present electrometric and analytical investigations confirm the formation and precipitation of cadmium ortho - $3CdO \cdot Sb_2O_5$ and pyro-$2CdO \cdot Sb_2O_5$ antimonates and cadmium ortho-thioantimonate, $3CdS \cdot Sb_2S_5$, in the vicinity of pH 7.9, 6.2 and 6.8, respectively. As their structures are not known they are represented in the form of double compounds.

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