Physico-chemical Studies on the Composition of Thiosulfates of Metals. I. Thermometric Studies of Bismuth Thiosulfate Complexes

By Mahendra Singh BHADRAVER

(Received April 11, 1962)

The composition of bismuth thiosulfate has been studied by the method of thermometric titrations between bismuth nitrate and sodium thiosulfate in aqueous and alcoholic medium. The direct titrations curve suggest the formation of $Na_3Bi(S_2O_3)_3$ in which the ratio of Bi : S_2O_3 is 1 : 3. In the reverse titrations also the formation of $Na_3Bi(S_2O_3)_3$ is indicated.

There is a meager amount of literature on the study of the composition of bismuth thiosulfate. Carnot and Hauser[1] suggested the formula $R_3Bi(S_2O_3)_3 \cdot nH_2O$ and he pointed out that the solutions of these salts contain $Bi(S_2O_3)^{3-}$ which breaks up readily. There is however hardly any reference in literature on the study of bismuth thionsulfate by physicochemical methods. Hence the present investigation by applying thermometric method was considered worthwhile.

In view of the difficulties associated with analytical work and to throw further light on the composition of bismuth thiosulfate, attempts have been made in this paper to study the composition of these complexes by thermometric method. With the results of potentiometric, conductometric and amperometric measurements in progress, the results of thermometric method have been incorporated and discussed in this paper.

Experimental

The Reagents used were of E. Merck quality. Standard solutions were prepared by weighing. In case of sodium thiosulfate few drops of chloroform were added during the preparation of the solution so that the solution may be serviceable for a longer time. The strength of the sodium thiosulfate solution was further checked by standard KIO_3 solution[2]. Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ was prepared by direct weighing and the solution was estimated as bismuth oxy-iodide[3].

The arrangement for thermometric titrations was the same as has been described by Naldar[4]. Using different concentrations of the two salts in solution,

1) O. Hauser, *Bull. soc. chim. France*, 35, 1 (1903).

2) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", p. 335.

3) A. I. Vogel, ibid., pp. 425 and 426.

4) B. C. Halder, *J. Ind. Chem. Soc.*, 23, 147 (1946).

TABLE I. SUMMARY OF THERMOMETRIC OBSERVATIONS

Table No.	Fig. No.	Curve No.	$Bi(NO_3)_3$ concn.	$Na_2S_2O_3$ concn.	Points Med.	Showing Calcd.	Breaks Obs.	Formula Supported	Ratio
Direct titration									
1	1	1	M/5	M/20 20 cc.	Aq.	1.66	1.6	$Na_3Bi(S_2O_3)_3$	1 : 3
2	1	2	M/5	18	Alc. 10%	1.50	1.5	$Na_3Bi(S_2O_3)_3$	1 : 3
3	1	3	M/5	16	20%	1.33	1.4	$Na_3Bi(S_2O_3)_3$	1 : 3
4	1	4	M/5	M/25 20	Aq.	1.33	1.4	$Na_3Bi(S_2O_3)_3$	1 : 3
5	1	5	M/5	18	Alc. 10%	1.20	1.2	$Na_3Bi(S_2O_3)_3$	1 : 3
6	1	6	M/5	16	20%	1.06	1.1	$Na_3Bi(S_2O_3)_3$	1 : 3
Reverse titration									
7	2	1	M/80 20 cc.	M/5	Aq.	3.75	3.7	$Na_3Bi(S_2O_3)_3$	3 : 1
8	2	2	18	M/5	Alc. 10%	3.375	3.4	$Na_3Bi(S_2O_3)_3$	3 : 1
9	2	3	16	M/5	20%	3.00	2.9	$Na_3Bi(S_2O_3)_3$	3 : 1
10	2	4	M/125 20 cc.	M/10	Aq.	4.80	4.8	$Na_3Bi(S_2O_3)_3$	3 : 1
11	2	5	18	M/10	Alc. 10%	4.32	4.30	$Na_3Bi(S_2O_3)_3$	3 : 1
12	2	6	16	M/10	20%	3.84	3.80	$Na_3Bi(S_2O_3)_3$	3 : 1

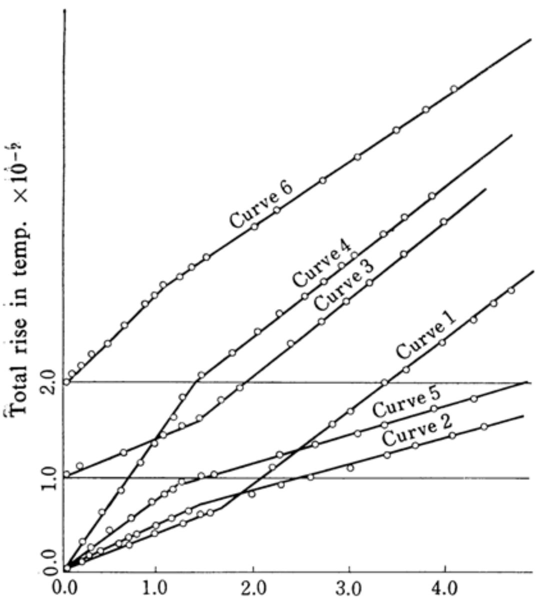

Fig. 1. Direct-titrations.
Curves 1, 2, 3 M/5 $Bi(NO_3)_3$ and M/20 sodium thiosulfate
Curves 4, 5, 6 M/5 $Bi(NO_3)_3$ and M/25 sodium thiosulfate

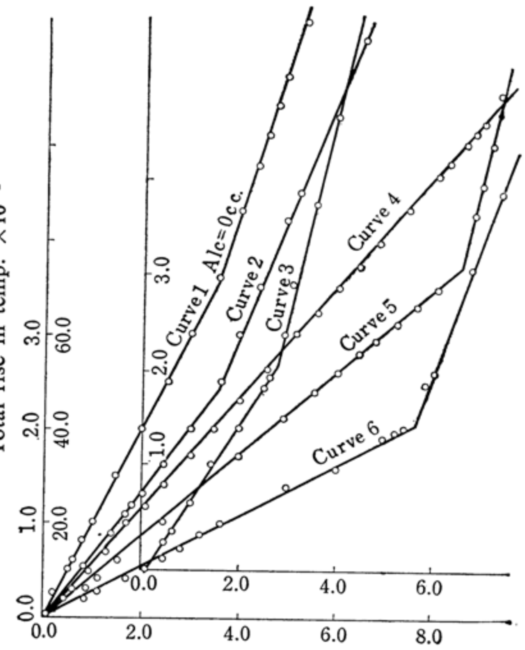

Fig. 2. Reverse-titrations.
Curve 1, 2, 3 M/5 sodium thiosulfate and M/80 $Bi(NO_3)_3$
Curve 4, 5, 6 M/10 sodium thiosulfate and M/125 $Bi(NO_3)_3$

the titrations were followed by the direct and reverse methods (i. e. when $Bi(NO_3)_3$) was added from burette to sodium thiosulfate solution in thermos flask and vice versa).

Titrations were also carried out in presence of alcohol up to 20% by volume. The total rise in temperature was then plotted against the titre in cc.

Discussion

It is evident from the summary of the observations of thermometric titrations that in the direct titrations the theoretical titre values required for the formation of $[Na_3Bi(S_2O_3)_3]$ would be (Table Nos. 1 to 6) 5.0, 4.5, 4.0, 2.0, 1.8 and 1.6 respectively in the ratio of 1 : 3. In the direct titrations one break occurs at the point of equivalence in the ratio 1 : 3. The theoretical values calculated for the reverse titrations accordingly for the ratio 1 : 1 are (Table Nos. 7 to 12) 1.25, 1.125, 1.00, 1.6, 1.44 and 1.28 respectively and therefore the theoretical titre values required for the ratio 3 : 1 would be 3.75, 3.375, 3.00, 4.80, 4.32 and 3.84 respectively. The observed values in the reverse titrations are in agreement with the values for the ratio 3 : 1. Thus the formation of the same compound $Na_3Bi(S_2O_3)_3$ is supported.

With a view to show the discrepancy between the observed and calculated titre values, a summary of observations in aqueous and alcoholic solutions is given above for comparison.

The results of our thermometric method are accurate and fairly support the views of Hauser[5].

Grateful thanks are due to Dr. J. N. Gaur, Maharaja College, Jaipur for his kind guidance in this piece of investigation.

Chemical Laboratories
Lohia College
Churu
Rajasthan, India

5) J. W. Mellor, "Treatise on Inorganic Chemistry", Vol. 10, p. 552.