Thermometric Studies on the Reaction between Silver Nitrate and Sodium Thiosulfate

By Mahendra Singh BHADRAVER

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Thermometric titrations between silver nitrate and sodium thiosulfate with varying concentrations of two salts in solution were performed. Reactions are indicated when Ag^+ and $S_2O_3^{2-}$ ions are present in solution in the molar ratio of 1 : 2, 1 : 1, 3 : 4 and 2 : 1 (in the direct method) and 1 : 2 and 1 : 1 (in the reverse method) respectively, indicating the formation of the complexes $Na_3Ag(S_2O_3)_2$, $NaAgS_2O_3$, $Na_5Ag_3(S_2O_3)_4$ and $Ag_2S_2O_3$ whereas in the reverse titrations $NaAgS_2O_3$ and $Ag_2S_2O_3$. The results support and throw more light on the reaction between silver nitrate and sodium thiosulfate.

There is meager amount of literatures on the study of this reaction. The possibility of formation of silver thiosulfate complexes was discovered by Herschel[1]. More recently Rosenheim and Steinhäuser[2] and Meyer and Eggeling[3] and lastly Rosenheim and Trewendt[4] carried out the study on the silver thiosulfate complexes. No attempt has so far been made by applying thermometric studies on this reaction. It was therefore considered worthy of interest to carry out study this reaction by thermometric method to throw more light on the nature of this reaction.

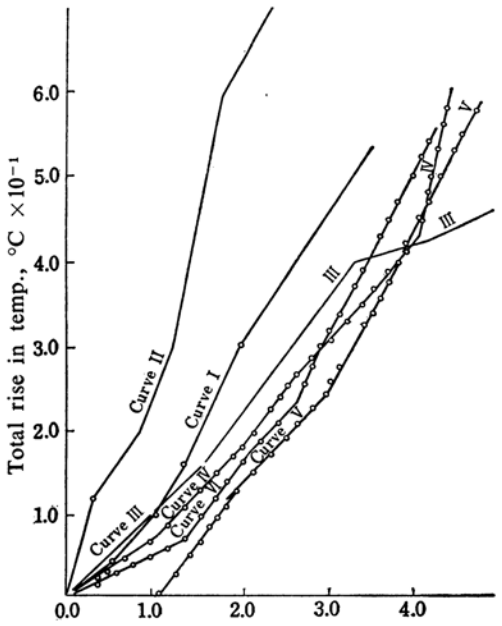

Fig. 1. Direct thermometric titrations curves for silver nitrate against sodium thiosulfate.
Curves I, II, III; M/5 $AgNO_3$ and M/100 $Na_2S_2O_3$
Curves IV, V, VI; M/10 $AgNO_3$ and M/100 $Na_2S_2O_3$ for curve IV, V, VI scale 1″=2 ml.

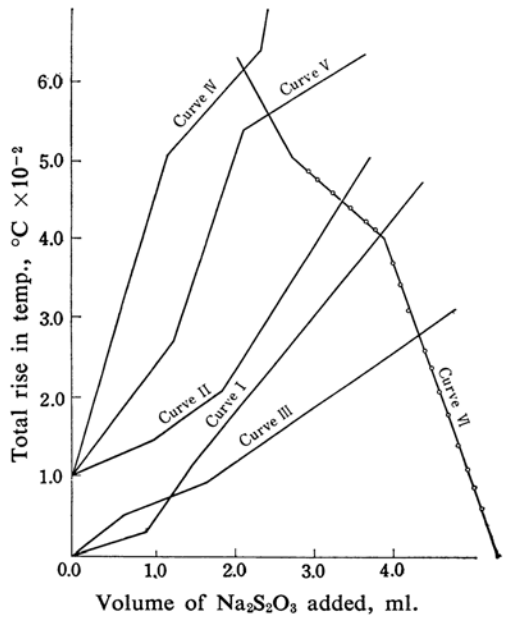

Fig. 2. Thermometric titrations curves for silver nitrate against sodium thiosulfate. (Reverse titrations) [Ag^+] conc. (molality or M)
Curve I, II, III; M/10 $Na_2S_2O_3$, M/200 $AgNO_3$
Curve IV, V, VI; M/40 $AgNO_3$; M/5 Na_2SO_3

Experimental

Silver nitrate and sodium thiosulfate employed for the preparation of solutions were of E. Merck quality. Thermometric titrations were carried out in the apparatus described by Dutoit[5]. Titrations

1) J. F. W. Herschel, *Edinb. Phil. Journal*, **26**, 2, 154 (1819).

2) A. Rosenheim and S. Steinhäuser, *Z. anorg. Chem.*, **25**, 72 (1900).

3) J. Meyer and H. Eggeling, *Ber.*, **40**, 1351 (1907).

4) A. Rosenheim and G. Trewendt, ibid., **61**, 1731 (1928).

5) P. Dutoit and E. Grobet, *J. Chim. Phys.*, **19**, 324 (1922).

were performed by the direct and reverse methods. Titrations were also carried out in varying percentage of alcohol upto a total concentration of 20% by volume. A correction was applied by carrying out 'blank' experiment using water instead of either reactants to account for the dilution effect.

Discussion

From the summary of observations in Table I it is clear that when silver nitrate is added to sodium thiosulfate, the reaction involves the formation of four different compounds $Na_3Ag(S_2O_3)_2$, $NaAgS_2O_3$, $Na_5Ag_3(S_2O_3)_4$ and $Ag_2S_2O_3$ respectively where the molar ratio of the reactants (silver nitrate and sodium thiosulfate) is 1 : 2, 1 : 1, 3 : 4 and 2 : 1 respectively. The reverse thermometric titration curves suggest that when the order of addition of reagents is reversed, the formation of the complexes $Ag_2S_2O_3$ and $NaAgS_2O_3$ takes place.

Rosenheim and Trewendt[4] have reported

TABLE I. SUMMARY OF THERMOMETRIC TITRATIONS

$AgNO_3$ concn.	$Na_2S_2O_3$ concn.	Med.	Point showing breaks		Formula supported	Ratio
			Calcd.	Obs.		
Direct titrations						
M/5	M/100	Aq.	0.50	0.50	$Na_3Ag(S_2O_3)_2$	1 : 2
			1.00	1.00	$NaAgS_2O_3$	1 : 1
			1.33	1.33	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			2.0	2.0	$Ag_2S_2O_3$	2 : 1
M/5	M/100	Alc. 10%	0.45	0.40	$Na_3Ag(S_2O_3)_2$	1 : 2
			0.90	0.90	$NaAgS_2O_3$	1 : 1
			1.2	1.2	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			1.8	1.8	$Ag_2S_2O_3$	2 : 1
M/5	M/100	Alc. 20%	0.8	0.8	$Na_3Ag(S_2O_3)_2$	1 : 2
			1.6	1.6	$NaAgS_2O_3$	1 : 1
			2.13	2.0	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			3.2	3.2	$Ag_2S_2O_3$	2 : 1
M/10	M/100	Aq.	1.0	1.0	$Na_3Ag(S_2O_3)_2$	1 : 2
			2.0	2.0	$NaAgS_2O_3$	1 : 1
			2.66	2.6	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			4.0	4.0	$Ag_2S_2O_3$	2 : 1
M/10	M/100	Alc. 10%	0.9	0.9	$Na_3Ag(S_2O_3)_2$	1 : 2
			1.8	1.8	$NaAgS_2O_3$	1 : 1
			2.4	2.4	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			3.6	3.6	$Ag_2S_2O_3$	2 : 1
M/10	M/100	Alc. 20%	0.8	0.8	$Na_3Ag(S_2O_3)_2$	1 : 2
			1.6	1.6	$NaAgS_2O_3$	1 : 1
			2.13	2.1	$Na_5Ag_3(S_2O_3)_4$	3 : 4
			3.2	3.2	$Ag_2S_2O_3$	2 : 1
Reverse titrations						
M/200, 20 cc.	M/10	Aq.	0.5	0.45	$Ag_2S_2O_3$	1 : 2
			1.0	1.0	$NaAgS_2O_3$	1 : 1
M/200, 18 cc.	M/10	Alc. 10%	0.45	0.42	$Ag_2S_2O_3$	1 : 2
			0.9	0.9	$NaAgS_2O_3$	1 : 1
M/200, 16 cc.	M/10	Alc. 20%	0.4	0.33	$Ag_2S_2O_3$	1 : 2
			0.8	0.8	$NaAgS_2O_3$	1 : 1
M/40, 20 cc.	M/5	Aq.	1.25	1.2	$Ag_2S_2O_3$	1 : 2
			2.5	2.5	$NaAgS_2O_3$	1 : 1
M/40, 18 cc.	M/5	Alc. 10%	1.12	1.1	$Ag_2S_2O_3$	1 : 2
			2.25	2.2	$NaAgS_2O_3$	1 : 1
M/40, 16 cc.	M/5	Alc. 20%	1.0	1.0	$Ag_2S_2O_3$	1 : 2
			2.0	2.0	$NaAgS_2O_3$	1 : 1

the formation of the complexes $NaAgS_2O_3 \cdot 1/2\ H_2O$, $Na_3Ag(S_2O_3)_2 \cdot H_2O$, and $Na_5Ag_3(S_2O_3)_4$. The formation of these complexes have been confirmed by our thermometric studies.

The possibility of the formation of the complexes $NaAg(S_2O_3)_2 \cdot H_2O$ as reported by Basset and Lemon[6] and $Ag_2S_2O_3 \cdot 4Na_2S_2O_3$ by Dey and Mushran[7] (by analysis) is ruled out by our thermometric studies.

Other physico-chemical methods are being tried for the study of this reaction and the results will be communicated in future.

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Chemical Laboratories
Lohia College
Churu, India

6) H. Basset, J. T. Lamon and Fritz Ephraim, "Text Book of Inorganic Chemistry", p. 584.
7) A. K. Dey and S. P. Mushran, *Proc. Nat. Acad. Sci.*, **16A**, 37 (1947).