

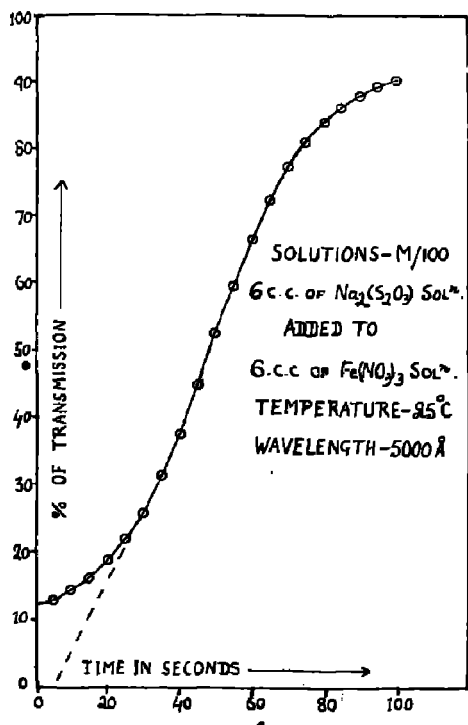
SPECTROPHOTOMETRIC STUDY OF THE FERRIC-THIOSULPHATE COMPLEX. PART I

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Determination of the formula of the labile coloured complex, formed by the reaction of thiosulphates with ferric salts, by the application of Job's method of continuous variation to the optical properties of the coloured complex has been reinvestigated due to the special nature of the decay curve. Three aqueous solutions of two ferric salts, one without acid and two others with different acid contents, have been used at two wave-lengths, 500 m μ and 600 m μ . The maximum absorption for the volume ratio of 1:1 of equimolecular solutions of ferric salt and thiosulphate without any acid confirms the formula Fe^+SO_3^- . The volume ratio changed to 1:2 and 1:3 according to the different acid contents. This has been explained as due to the difference between the effective concentration and the actual concentration of $\text{S}_2\text{O}_3^{2-}$ ion. When acidic solutions of ferric salts were used, the absorptions at zero-time for wave-lengths 500 m μ and 600 m μ were not much different. But with solutions containing no acid, the difference was very high. The increase in absorption in case of aqueous solutions containing no acid at lower wave-length region is ascribed to the polynuclear hydrolysis product $\text{Fe}(\text{OH})_3\text{Fe}^{3+}$. Indication for the existence of $\text{Fe}(\text{OH})_3\text{Fe}^{3+}(\text{S}_2\text{O}_3)$ has also been given.

A coloured intermediate is produced by the reaction of thiosulphates with ferric salts.

FIG. 1



The curve representing the rate of decay of this coloured intermediate, as obtained by the plot of the percentage of transmission against time, was found to be of S-shape (Patnaik and Mahapatra, *Curr. Sci.*, 1955, 24, 195). This is contrary to the observations of Haldar and Banerjee (*Proc. Nat. Inst. Sci.*, 1948, 14, 1) and that of Page (*Trans. Faraday Soc.*, 1953, 49, 635) who used optical methods for assigning the formula $\text{Fe}^+\text{S}_2\text{O}_3^-$ to this coloured complex. For the application of Job's method of continuous variation (*Ann. chim.*, 1928, 2, 9, 113) to the determination of the formula of the coloured complex, the absorption due to the complex just at the moment of mixing the solutions of ferric salt and thiosulphate has to be evaluated. This is done by extrapolation of the decay curve to zero-time. Since the extrapolation value depends solely on the nature of the curve, our S-shaped curves are bound to provide different values from those of Haldar and Banerjee, and of Page. It can be seen from Fig. 1, that any endeavour to extrapolate the curve, neglecting the first

few points up to the point of inflection, would give rise to negative transmission which cannot be accepted because of the fact that the solution cannot have negative transmission value at zero-time. Thus, reinvestigation of the application of the Job's method to the determination of the formula spectrophotometrically became necessary.

EXPERIMENTAL

Unicam diffraction-grating spectrophotometer (Model 350) was used. The wave-length was calibrated by the dyodinium-filter supplied with the instrument. Particular care was taken to see that the intensity of the light beam did not change during the course of a run which was of not more than a few minutes' duration, mostly 100 seconds. The checking was done by comparing at the end of each run with the standard cell containing water for 100% transparency.

Quick-delivery pipettes were specially prepared so that the time of delivery of the solution did not last for more than 1.3 seconds. Stirring by hand was carried with a special stirrer for 2 to 3 seconds. At the end of the 5th second readings were taken. The reliability of the first reading at the 5th second was verified by a dichromate solution for 3 seconds and then noting the % transmission at the end of the 5th second, which was the same as the one taken without stirring. All the cells used were calibrated to provide the same transparency with standard one.

Ferric salts and sodium thiosulphate were of E. Merck Extra Pure quality or B.D.H. Analar quality. Hydrochloric and nitric acids used were of Schering-Kahlbaum 'Pro-analysi' quality. All other reagents used for standardisation were of E. Merck Extra Pure quality. Since copper contamination accelerated the rate of decay, triple-distilled water in all-pyrex distillation set was used.

Thiosulphate solution was standardised against standard potassium iodate solution. Solutions of ferric salts were standardised iodimetrically (Patnaik and Mahapatra, unpublished).

A thermostat was maintained at 25° with fluctuation of $\pm 0.1^\circ$. All solutions for use were kept in stoppered Erlenmeyer flasks in the thermostat. It was observed that the rise of temperature for a run lasting 3 minutes was 0.2° .

Three solutions of ferric salts in water, one without acid and the other two having corresponding acid concentrations of 0.1M and 0.25M were used. The concentrations of Fe^{3+} and of $\text{S}_2\text{O}_3^{2-}$ in their respective solutions (not the effective concentration in the mixture) were each of 0.01M strength. For the application of Job's method, the composition of the mixture was varied in the manner, 11:1, 10:2, 2:10, 1:11, the total volume being always 12 c.c. In Table I the readings recording the rate of decay for a set of three mixtures of different compositions are shown at two wave-lengths. For economy of space 110 such readings have not been recorded here.

In Tables II and III the % transmissions at zero-time have been recorded for mixtures of different compositions of the two ions at the two wave-lengths, 500m μ and 600m μ . Due to rapid hydrolysis of aqueous solutions of ferric salts, very fresh solutions were used for experiments.

TABLE I

Temperature = $25^{\circ} \pm 0.1^{\circ}$

Time.	6 c.c. of 0.01M- $\text{Na}_2\text{S}_2\text{O}_3$ soln. added to 6 c.c. of 0.01M- $\text{Fe}(\text{NO}_3)_3$ soln. without acid.		8 c.c. of 0.01M- $\text{Na}_2\text{S}_2\text{O}_3$ soln. added to 4 c.c. of 0.01M- $\text{Fe}(\text{NO}_3)_3$ soln. containing 0.1M- HNO_3 .		9 c.c. of 0.01M- $\text{Na}_2\text{S}_2\text{O}_3$ soln. added to 3 c.c. of 0.01M- $\text{Fe}(\text{NO}_3)_3$ soln. containing 0.25M- HNO_3 .	
	% Transmission at		% Transmission at		% Transmission at	
	500 m μ .	600 m μ .	500 m μ .	600 m μ .	500 m μ .	600 m μ .
5 sec.	13.00	26.25	21.50	23.00	38.00	39.50
10	14.50	28.50	24.25	25.75	39.75	41.00
15	16.25	30.75	28.00	29.75	43.25	43.25
20	18.75	34.00	32.75	35.25	46.00	45.75
25	22.00	37.75	39.25	42.25	48.75	48.50
30	25.75	43.25	47.00	49.75	51.25	51.50
35	31.50	48.75	54.25	57.75	56.75	54.25
40	37.50	54.75	61.75	64.50	59.50	57.00
45	44.75	61.25	68.00	70.50	62.00	60.00
50	51.50	67.50	73.25	75.50	64.50	62.75
55	59.50	73.50	77.75	79.75	66.00	65.50
60	66.50	79.00	81.25	83.00	69.00	67.75
65	72.50	83.50	83.50	85.25	70.75	70.25
70	77.50	86.75	86.00	87.25	72.75	72.25
75	81.25	89.50	88.00	88.75	74.50	74.50
80	84.25	91.50	89.00	90.25	75.75	76.50
85	86.25	92.50	90.00	91.25	77.50	77.75
90	88.00	94.00	91.00	92.25	78.50	79.25
95	89.50	94.50	92.00	92.75	80.00	80.50
100	90.25	...	92.75	93.50	80.75	81.50

TABLE II

% Transmission at zero-time of $\text{Fe}(\text{NO}_3)_3$ solution.Temp. = $25^{\circ} \pm 0.1^{\circ}$.

Comp. of soln. (c.c.)		Fe solns. without acid.		Fe solns. with 0.1M- HNO_3 .		Fe solns. with 0.25M- HNO_3 .	
Fe^{3+}	$\text{S}_2\text{O}_3^{2-}$	500 m μ .	600 m μ .	500 m μ .	600 m μ .	500 m μ .	600 m μ .
11	1	48.50	68.00	76.50	77.75	89.00	89.00
10	2	31.00	49.75	59.75	62.00	79.00	81.00
9	3	21.25	37.00	46.75	49.00	69.50	71.50
8	4	15.75	30.00	38.00	39.25	62.00	63.50
7	5	13.00	26.25	29.00	31.50	54.50	56.00
6	6	12.25	25.25	25.75	26.50	48.75	49.50
5	7	15.00	26.75	22.25	22.50	43.25	45.00
4	8	18.00	32.00	20.25	21.50	39.00	40.20
3	9	27.25	42.50	22.50	23.50	31.00	38.25
2	10	40.25	55.75	29.00	31.00	38.50	39.50
1	11	66.25	77.50	49.50	51.00	52.00	53.50

TABLE III

% Transmission at zero-time of FeCl_3 solution.Temp. = $25^\circ \pm 0.1^\circ$.

Comp. of soln (c.c.) $\text{Fe}^{3+} : \text{S}_2\text{O}_3^{2-}$		Fe solns. without acid.		Fe solns. with 0.1M-HCl.		Fe solns. with 0.25M-HCl.	
		500 m μ .	600 m μ .	500 m μ .	600 m μ .	500 m μ .	600 m μ .
11	1	50.75	68.50	78.50	81.75	88.50	92.00
10	2	32.25	50.00	64.75	67.00	81.75	85.00
9	3	22.75	37.50	52.50	56.00	75.75	78.25
8	4	17.50	31.50	44.00	46.75	69.00	71.25
7	5	15.00	27.25	35.50	37.75	61.75	64.50
6	6	14.50	26.00	30.50	32.50	56.25	59.25
5	7	16.50	28.50	26.75	28.25	50.25	53.25
4	8	20.25	33.25	24.25	27.00	46.00	48.25
3	9	27.75	42.50	26.50	28.25	43.25	45.25
2	10	41.25	57.00	33.25	35.00	44.00	45.00
1	11	66.75	78.50	52.25	53.75	55.50	55.75

DISCUSSION

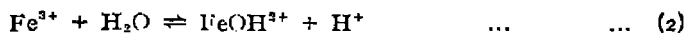
From Tables II and III the % transmission at both the wave-lengths appears to be minimum for the mixture of equal composition when solutions containing no acid of both ferric salt and aqueous solution of thiosulphate are used. This suggests the formula $\text{Fe}^+\text{S}_2\text{O}_3^-$ for the coloured complex and confirms the observation of Halder and Banerjee (*loc. cit.*). In case of the solutions of ferric salts containing 0.1M acid, the minimum was found for a mixture of 4 c.c. of ferric salt solution and 8 c.c. of thiosulphate solution. For acid content of 0.25M in the solution of ferric salts, the minimum was observed for the ratio of 3:9. The experiments with acid solutions would ordinarily suggest such formulae as $\text{Fe}(\text{S}_2\text{O}_3)_2^-$ and $\text{Fe}(\text{S}_2\text{O}_3)_3^{2-}$ for the coloured complex under different H^+ concentrations. In aqueous solution of sodium thiosulphate, except for the ion pair $\text{Na}^+\text{S}_2\text{O}_3^-$ present to a very small extent, almost the whole of $\text{S}_2\text{O}_3^{2-}$ ions are available for formation of the complex according to the following reversible reaction, suggested by Schmid (*Z. physikal. Chem.*, 1930, 148, 321):



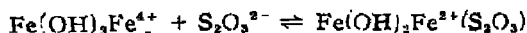
However, with the increase in the concentration of H^+ ion, it is known that more and more of the ion pair HS_2O_3^- is formed, thereby leaving less and less of free $\text{S}_2\text{O}_3^{2-}$ for the above reversible reaction. So the effective concentration of the $\text{S}_2\text{O}_3^{2-}$ ion is not the same as its total concentration. Thus, the change of the ratio from 1:1 to 1:2 or 1:3 is explained without having to ascribe such formulae as $\text{Fe}(\text{S}_2\text{O}_3)_2^-$ and $\text{Fe}(\text{S}_2\text{O}_3)_3^{2-}$ for the labile coloured intermediate. However, in a subsequent communication, a direct and simple experimental evidence will be furnished to prove beyond doubt that the labile coloured complex possesses the formula $\text{Fe}^+\text{S}_2\text{O}_3^-$.

Hajdar and Banerjee (*loc. cit.*) worked with aqueous solutions, while Page (*loc. cit.*) with acidic solutions. When our results obtained with aqueous as well as acidic solutions, as recorded in Tables II and III, are scrutinised, it can be seen that in case of aqueous solution without acid the % transmission at zero-time increases very considerably when the wave-length is changed from 500 m μ to 600 m μ . Further, it can be noticed that the difference between the transmissions at the two wave-lengths decreases with decrease in the volume of the solution of ferric salt and increases again, showing that the difference is dependent on both the solutions of the ferric salt and the thiosulphate. In case of acidic solutions of ferric salts, no such marked change in the % transmission with the change of wave-length occurred, and further difference between the two % transmissions was more or less the same. The minimum transmission or maximum absorption for aqueous solutions though occurs at 6:6 composition ratio of $\text{Fe}^{3+}:\text{S}_2\text{O}_3^{2-}$, yet the absorption of 7:5 ratio (higher Fe^{3+}) is very much nearer to it than that of the 5:7 ratio (higher $\text{S}_2\text{O}_3^{2-}$). The question now arises as to the reason for the marked change in the transmission in case of aqueous solution without acid due to the change in the wave-length. Formation of some complex would explain for such a change in absorption. But the formation of any new complex at zero-time to any considerable extent would not allow the composition ratio of 6:6 to afford the maximum absorption. So it leads to the inescapable conclusion that some complex is formed in very low concentration having high extinction coefficient.

In solutions of ferric salts the following equilibria are known to exist (Milburn and Vosburgh, *J. Amer. Chem. Soc.*, 1955, 77, 1352),



reaction (3) preponderating at higher concentrations of Fe^{3+} ion over reaction (2). It is evident that with the increase in concentration of H^+ , the concentration of FeOH^{2+} would correspondingly decrease, and consequently the concentration $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$. So in aqueous solution the concentration of this complex $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$ would be the maximum. Due to the association of two ferric ions, this complex would possess high extinction coefficient at lower wave-length region. In fact 60% of the differences is accounted for by the aqueous solution of the ferric salt at the required concentration. And since difference in absorption is also dependent on the volume of thiosulphate solution, it is under investigation whether the following reversible reaction



can also be taken into account along with reaction (3). The existence of these complexes would also explain the reason for no marked change in % transmission when acidic solutions were used. Also these would explain the dependence of the difference of absorption on the concentration of Fe^{3+} , OH^- and $\text{S}_2\text{O}_3^{2-}$ ions. It has been noted from the experimental data recorded in Tables II and III that in case of aqueous solution

of ferric salts the absorption for the composition ratio 7:5 (higher Fe^{3+}) has almost the same absorption as the composition ratio 6:6, while that for the composition ratio 5:7 (higher $\text{S}_2\text{O}_3^{2-}$) is away from the absorption for the composition ratio 6:6. This is also explained as two Fe^{3+} ions and either one or none of the $\text{S}_2\text{O}_3^{2-}$ ions are concerned in the formation of the complex or complexes responsible for stronger absorption in the shorter wave-length region of the visible range.

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