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Study of Thio Salts. Part III. Thio and Thio-oxy Salts of Tin(IV)

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Stability constant of thio-anion, SnS_3^{2-}, and elucidation of the composition of thio-oxy-anion of Sn(IV) have been made from the study of the dissolution of stannic sulphide in sodium hydrosulphide, Na_2S, and NaOH by solubility, conductance, and potentiometric measurements.

Stannic sulphide dissolves in caustic alkalies, alkaline carbonates, ammonia, and ammonium carbonate and also in alkaline sulphides[1]. The dissolution of stannic sulphide in alkaline medium has been explained on the basis of formation of stannates, thio-oxy-stannates, and thiostannates, but the composition of these complexes has not been conclusively proved. Only recently Baliko and Lisetskaya[2] have reported the formation of SnS_2OH^- ion by study of the solubility of stannic sulphide in acetate-ammonia buffer. They further reported that the dissolution of stannic sulphide in alkaline solution containing hydrogen sulphide was due to the formation of a thio salt of tin and the composition of the thio-anion as SnS_3^{2-}. On the basis of the formation of the thic-anion of tin, an analytical method for estimating tin has been developed by Taimni and Agrawal[3].

The present paper deals with the dissolution study of stannic sulphide in sodium hydrosulphide, sodium sulphide, and sodium hydroxide to determine the stability constant of the thic-anion SnS_3^{2-} and to elucidate the composition of the thio-oxy-anion of Sn(IV). The methods employed are based on solubility, conductivity, and potentiometric measurements.

EXPERIMENTAL

A R. grade stannic chloride solution was treated with an excess of sodium sulphide. From this solution stannic sulphide was precipitated by adding an excess of acetic acid. The precipitate was washed till the wash water was free of soluble impurities. The precipitate was then suspended in distilled water and kept in a stoppered Jena bottle. The supernatant water was found to be neutral.

After shaking well, a measured quantity of the suspension was taken out and filtered through a sintered glass crucible, washed twice with absolute ethanol and ether, finally suck-dried, and weighed as $SnS_2 . 2H_2O$. It was found that 10 ml of the sulphide suspension, thus estimated gave practically the same amount of the solid residue.

For preparing solutions of either sodium sulphide or sodium hydrosulphide, purified hydrogen sulphide was passed in a standardised sodium hydroxide solution for about 20

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[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 7, p. 472.

[2] Baliko and Lisetskaya, *Zhur. Neorg. Khim.*, 1956, **80**, 1969.

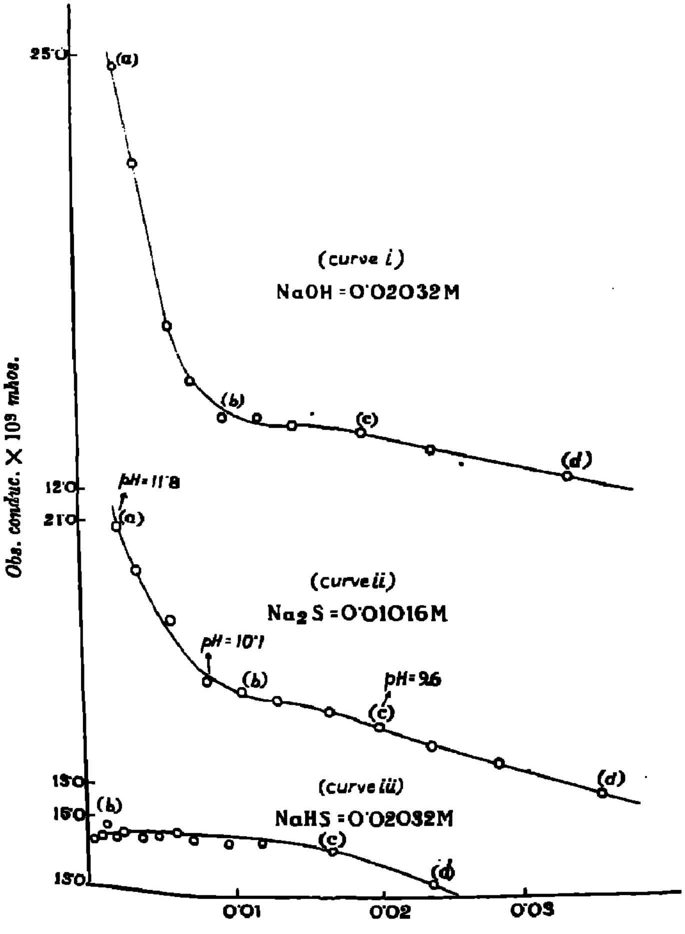
[3] Taimni and Agrawal, *Anal. Chim. Acta*, 1953, **205**.

minutes. The amount of hydrogen sulphide in the solution was estimated iodometrically. The ratio of Na to S was adjusted to 2:1 in case of sodium sulphide and 1:1 in case of sodium hydrosulphide by adding requisite amount of alkali to this solution.

Conductometric Study

Fig. 1 (curves *i-iii*) records our results on the measurement of the conductance of the solutions of sodium hydroxide, sodium sulphide, and sodium hydrosulphide respectively containing different amounts of stannic sulphide added in g. moles. In Fig. 2 are noted the variation in conductance of a solution of stannic sulphide in NaOH by adding different amounts of HCl. The measured *p*H values of the solutions at the points 'a', 'b', 'c', and 'd' in the curves given in Figs. 2 and 1 are also noted.

It will be seen from Fig. 1, curves (*i*) and (*ii*) that with increasing amounts of tin sulphide added, there is first a rapid drop in electrical conductance of both NaOH and Na_2S solutions.



$Sn\ S_2$ *present in g. moles.*

FIG. 1

It is furthr seen in Fig. 1 (*i*) that there is one sharp break at (b), where the stoichiometric relation of SnS_2 to NaOH is 1:2, and the other, though less sharp but perceptible, is at the point 'c', where the stoichiometric relation of SnS_2 to NaOH is 1:1. Beyond 'c' there is a very slight decrease in conductance, but a yellow colour of the solution appears here, which gradually goes on increasing. The yellow solution is found to be stannic sulphide in colloidal state as this can be quickly coagulated by neutral electrolytes like KCl. It appears therefore that the reaction between stannic sulphide and NaOH occurs in the following way:

$$SnS_2 + 2OH^- \rightleftharpoons SnS_2O^{2-} + H_2O \quad .. \quad .. \quad (1)$$

$$H_2O + SnS_2 + SnS_2O^{2-} \rightleftharpoons 2HSnS_2O^- \quad .. \quad .. \quad (2)$$

The thio-oxy compounds yield colorless solutions before the point 'c'.

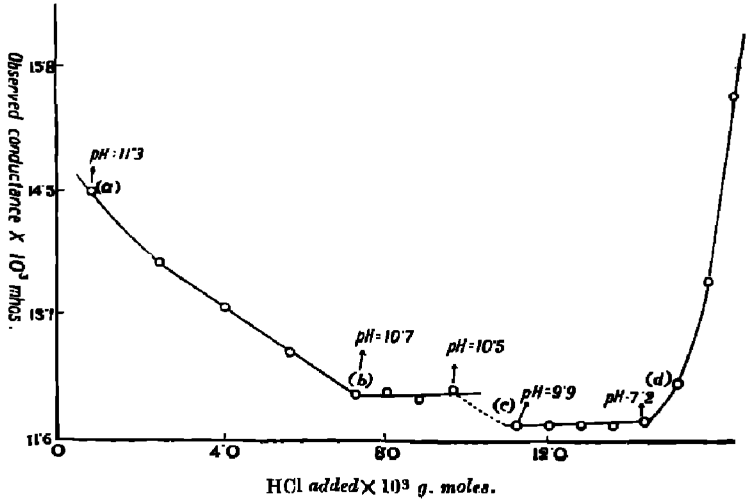


FIG. 2. Mixture containing 0.01625 *M*-NaOH and 0.00471 *M*-SnS_2.

In Fig. 2 the variation in the conductance, obtained by addition of different amounts of HCl to a thio-oxy stannate solution in an excess of alkali, has been reproduced. It is clear that there is a rapid fall in conductance in earlier stages due to neutralisation of the excess of alkali present. This proceeds to the point 'b' where the ratio of unused NaOH to SnS_2 becomes 2:1. Beyond this the anion SnS_2O^{2-} reacts with acid as:

$$SnS_2O^{2-} + H^+ \rightleftharpoons HSnS_2O^- \quad .. \quad .. \quad (3)$$

The above reaction is completed at the point 'c' where the ratio of unused alkali to stannic sulphide approaches 1:1. Further addition of the acid leads to the reaction:

$$HSnS_2O^- + H^+ \rightleftharpoons SnS_2 + H_2O \quad .. \quad .. \quad (4)$$

This continues to the point 'd' where the amount of acid added is approximately equivalent to the total amount of alkali used in the experiment. The 'bc' and 'cd' portions of the curve, separated at the point 'c', are flat, suggesting the titration of a weak dibasic acid in steps. In other words, these portions represent the titration of the salts, Na_2SnS_2O and $NaHSnS_2O$, by a strong acid resulting in the formation of a weak acid and sodium chloride. Hence there is hardly any variation in conductance in this region.

Stannic sulphide is obtained from reaction (4) which starts from 'c'. From here stannic sulphide appears in colloidal state, as is evident from the colour of the solution, which changes from colorless to yellow, orange, red-yellow. The coagulation of the colloidal stannic sulphide completes at the point 'd'. There is a sharp increase in conductance beyond the point 'd' due to appearance of free HCl after neutralisation of the alkali present.

Fig. 1 (*ii*), which refers to the solution obtained by adding stannic sulphide to a sodium sulphide solution, is similar to Fig. 1(*i*) showing one break in the curve at the point 'b' where the stoichiometric ratio of stannic sulphide to sodium sulphide is 1:1. The point 'c' in the curve with ratio 1:0.5 for the two components indicates the appearance of a yellow colour. Possible reactions taking place in the dissolution of stannic sulphide in Na_2S are:

$$SnS_2 + S^{2-} \rightleftharpoons SnS_3{}^{2-} \quad .. \quad .. \quad (5)$$

$$SnS_3{}^{2-} + SnS_2 + H_2O \rightleftharpoons HSnS_2O^- + HSnS_3{}^- \quad .. \quad (6)$$

Where the ratio of SnS_2 to S^{2-} is 1:1, majority of the thio-anion formed is according to equation (5). Further, it is seen that when a larger amount of stannic sulphide is added, the dissolution of stannic sulphide continues till the ratio of SnS_2 to S^{2-} is 1:0.5. Hence the second stage of dissolution is given by equation (6). We conclude this because the solution remains colorless to the point 'c' where the ratio of SnS_2 to S^{2-} is 1:0.5. Beyond the point 'c', where the ratio of SnS_2 to S^{2-} exceeds 1:0.5, the excess of stannic sulphide appears in colloidal state, which is visually observable.

Fig. 1 (*iii*) represents the conductance measurement by the gradual addition of stannic sulphide in a solution of NaHS. Readings were taken after the solutions were kept for 24 hours in stoppered flasks. Hardly any perceptible change in electrical conductance was found. A yellow-coloured solution is immediately produced by the addition of stannic sulphide to a hydrosulphide solution, suggesting the formation of colloidal stannic sulphide and it gradually fades with time. Very dilute sodium hydrosulphide solution appears to react slowly with stannic sulphide according to the equation:

$$SnS_2 + HS^- \rightleftharpoons HSnS_3{}^- \quad .. \quad .. \quad (7)$$

A study of the *p*H values noted in the curves shows that the thio-oxy anion, SnS_2O^{2-}, is stable above *p*H 10.7 and thio-anion, $SnS_3{}^{2-}$, above *p*H 10.2, whereas $HSnS_2O^-$ is stable in the range of *p*H 10.7-9.8. It is further seen that colloidal SnS_2 is stable in the range of *p*H 9.4 to 7.0 as precipitation of the sulphide starts from *p*H 7.0.

Dissolution Study of Stannic Sulphide

For the dissolution study, reaction mixtures were prepared in 250 ml bottles by taking a constant volume of stannic sulphide suspension and mixing it with varying amounts of sodium hydrosulphide. To every reaction mixture a constant volume of KCl solution was added in order to coagulate any colloidal stannic sulphide formed. Each bottle was well shaken for half an hour and kept overnight at a constant temperature. The supernatant solution was then sucked out and Sn (IV) was estimated in it by the thio-salt method. The results obtained are recorded in Table I. In column 6, the concentration of sulphide ions, which are present in the hydrosulphide solution, has been calculated using the known dissociation constant value of hydrogen sulphide. Assuming that all tin sulphide in the dissolved state is $HSnS_3^-$, the concentration ratio $[HSnS_3^-]/[HS^-]$ is calculated and noted in the last column. The concentration of the electrolytes in the solution is sufficiently high and slight variations, which may occur due to changes in ionic strength, have been neglected for the purpose of calculations mentioned above.

TABLE I

NaHS solution $=0.9488\,M$. SnS_2 susp. $=0.0622\,M$ (25 ml taken). KCl solution $=0.1000\,M$. Total vol. $=50.0$ ml. Temp. $=25°$.

NaHS soln.	KCl soln.	HS^-.	SnS_2.	HS^- left after formation of SnS_3^{2-}.	$\frac{(HSn\,S_3^-)}{(HS^-)}$.
3.0 ml	10.0 ml	0.05687 *M*	0.01133 *M*	0.04553 *M*	2.5×10^{-1}
5.0	10.0	0.09461	0.01793	0.07668	2.3×10^{-1}
7.0	10.0	0.13280	0.02286	0.10990	2.1×10^{-1}
8.0	10.0	0.15180	0.02816	0.12360	2.3×10^{-1}
10.0	10.0	0.18980	0.02956	0.16020	1.8×10^{-1}
12.0	10.0	0.22780	0.03139	0.19640	1.6×10^{-1}

The average value obtained for the concentration ratio $[HSnS_3^-]/[HS^-]$, *i.e.*, K_s, may be taken as equal to 2.1×10^{-1}. This is evidently the conventional equilibrium constant for the reaction:

$$SnS_2 + HS^- \rightleftharpoons HSnS_3^-$$

The decomposition of thio salt resulting in the precipitation of stannic sulphide may be expressed as:

$$HSnS_3^- + H_2O \rightleftharpoons H_2S + OH^- + SnS_2$$

The value for this equilibrium constant, *i.e.*, hydrolysis constant of the thioanion, is obtainable from the relation $K_h(HS^-)\,/\,K_s(HSnS_3^-)$, taking the effective mass of the slightly soluble stannic sulphide constant. In the above equation, $K_h(HS^-)$ is the hydrolysis constant of HS^- and $K_s(HSnS_3^-)$ denotes the stability constant of $HSnS_3^-$. With the help of this equation, the stability of varying amounts of thio-anion at different *p*H's of hydrosulphide solution has been calculated and the values are recorded in Table II.

TABLE II

$(HSnS_3^-)$ (stable)	..	1.00	0.10	0.01	0.001	0.0001
*p*H	..	10.9	10.4	9.9	9.4	8.9

This value of hydrolysis constant is related to the true value for hydrolysis of the thio-anion resulting in the formation of the acid, H_2SnS_3, by two more equilibria. One is the solubility of the sulphide in water and the other, decomposition of the acid resulting in the formation of tin sulphide and hydrogen sulphide. Further discussion on these equilibria will be communicated later on.

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